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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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Process for producing ultrafine mixed oxide powders

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Field of the Invention

The invention relates to methods of producing ultrafine powders of mixed oxides of perovskite or spinel structure as well as the ultrafine mixed oxide powders produced and methods of making them into bodies.

- 5 Perovskites are mixed oxides of structure ABO_3 and spinels are mixed oxides of structure $A_xB_yO_4$ where A and B are metals of valences suitable to form compounds of the given structures, and where x/y is 0.2, 0.5, 1.25 or 3.5 depending on the metal valences. The invention also pertains to ultrafine powders made of solid solutions and doped compounds of perovskite and spinel structures.
- 10 Various example of the perovskites and spinels to which the invention applies will be exemplified below. However, for clarity of the disclosure the invention will be described by way of example mainly in relation to the perovskite barium titanate $BaTiO_3$ as well as solid solutions and doped compounds derived from barium titanate.

Background of the Invention

- 15 Barium titanate is an important material for the electronic industry due to its dielectric and piezoelectric properties which make it suitable for many applications such as multilayer ceramic capacitors, positive temperature coefficient (PTC) thermistors, piezoelectric actuators, passive memory storage devices, acoustic transducers, and in electroluminescent panels.
- 20 The market for multilayer ceramic capacitors (MLCC) continues to demand smaller size components for a given capacitance or increased capacitance within a given part design. The capacitance per unit volume for an MLCC can be derived as:

$$C_v = n K_0 K / t^2$$

- where C_v is capacitance per unit volume of the active part of the capacitor, n is the
25 number of active layers, K_0 is the permittivity of free space (a constant), K is the

dielectric constant of the ceramic and t is the active thickness separating the active layers. In a given MLCC design with a fixed active volume C_v has to be increased by:

- (1) Using a ceramic with higher K
 - (2) Making thinner layers, t
 - 5 (3) Using more layers, n , in the component
 - (4) A combination of the above
-

Option (2) is an effective way to increase C_v and thinner layers of both ceramic and electrode are required to realize the benefit of more layers (3).

For use in smaller size MLCC as described above, the following characteristics are
10 required for barium titanate powder:

- Small particle size
- Isotropic shape
- Narrow particle size distribution with limited agglomeration
- No agglomerates bigger than the thickness of the dielectric layers of the MLCC.
- 15 - Controlled stoichiometry with ideal Ba/Ti ratio very close to 1
- High purity
- High density tetragonal phase

Small particle size is required to design MLCC with dielectric layers smaller than 1 micron in thickness. At least 5 pieces of grains are required between the electrodes to
20 ensure long term stability to the final product; therefore fine grains of less than 200nm are required for a ceramic layer, which is as thin as 1 micron or less. Small particle size also allows sintering at lower temperature than the usual range 1250-1350°C (this behaviour is also useful when the ceramic is co-fired with palladium-silver alloys or nickel or copper which have a low melting temperature.)

25 A narrow particle size distribution allows achieving porosity free and homogeneous microstructure after sintering the ceramic layer. It is well known that narrow particle size distributions and well-dispersed suspensions are required to manufacture pastes for

screen-printing or tape casting. Agglomerates bigger than the thickness of the dielectric layers of the MLCC are detrimental to obtaining adequate MLCC.

Controlled stoichiometry with Ba/Ti ratio close to 1.000 is necessary to obtain excellent electrical properties and well-defined sintering behaviour. The Ba/Ti ratio also affects the sintering temperature. The presence of excess TiO_2 , as it forms a eutectic liquid phase with BaTiO_3 at 1332°C , is known to dramatically influence the microstructure development. The presence of secondary phase $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ leads to the degradation of the insulation resistance at high temperature. Decreasing Ba/Ti ratio from 0.999 to 0.993 can lead to grain sizes twice bigger after sintering.

10 High purity powder is required to control the dielectric properties of barium titanate.

Better dielectric properties are obtained from high-density barium titanate with a tetragonal structure. Tetragonal barium titanate powders have a better sintering behaviour, higher intrinsic density and lead to ceramics with higher dielectric constants than cubic-phase powders. Also, cubic-phase barium titanate produced by the hydrothermal route exhibits a bloating effect when the MLCC is sintered, causing severe cracks and delamination, as a result of the segregation of porosity in the electrode region.

20 Various methods are used for the production of barium titanate and other mixed oxides of perovskite or spinel structure. In order to obtain above mentioned required characteristics, an economically acceptable process or method of production of barium titanate should use low cost equipment and raw material, limit grinding or pulverizing processes, use low temperature, and have short production time.

25 Traditionally mixed oxides are prepared using the solid-state route. In the case of barium titanate, it is prepared by ball milling BaCO_3 and TiO_2 . The mixture is then heated at a temperature of 900°C or above. However, BaTiO_3 prepared at high temperature exhibits some drawbacks, such as large particle size, a wide size distribution, and a high impurity content resulting from repetitive calcinations and

grinding treatments. Further limitations include the inability to control stoichiometry and crystallinity. Often an undesired secondary phase such as BaTi_2O_5 is produced.

Other techniques, such as precipitation, gas condensation, and sol-gel processing, have been developed to improve size, size distribution, and purity. As an example, the sol-gel processing using metal alkoxides as reactants leads to fine particles but alkoxides are generally too expensive. The oxalate co-precipitation route consisting of precipitation of a mixed barium-titanium oxalate precursor by reaction between a BaCl_2 and TiCl_4 solution and an oxalic acid solution requires heat-treatment ($\sim 700^\circ\text{C}$) with the common drawbacks of large particle size, wide particle size distribution and agglomeration.

Hydrothermal synthesis is another wet chemical route to prepare barium titanate. Usually a barium soluble salt (e.g. chloride, nitrate, acetate) or barium hydroxide is used as barium precursor. Titanium is usually provided by titanium dioxide or amorphous titanium hydroxide (prepared by hydrolysing organic or inorganic titanium compounds). Often, NaOH or KOH are used as mineralising agent. The reactants are subjected to high temperatures and pressures in an autoclave. Using amorphous titanium hydroxide generally leads to a wider particle size distribution and agglomerates, and requires higher cost raw materials. Using TiO_2 as precursor leads to a narrower particle size distribution but it is difficult to achieve an adequate Ba/Ti ratio and the necessary longer production time increases the level of agglomeration and the cost of the process. In general in a large hydrothermal reactor it is difficult to ensure homogeneous nucleation conditions within the whole vessel, which in turn induces a wide size distribution.

Another drawback of a hydrothermal synthesis at moderate temperatures is that it leads to cubic-phase barium titanate with a low density. Hydrothermal conditions for producing commercial quantities are usually under maximum temperature of 350°C and pressures below 100 Mpa, above which conditions are considered severe (Riman et al., Hydrothermal crystallization of ceramics, *Ann. Chim. Sci. Mat.*, 27(6), pp 15-36, 2002). However, in order to obtain a higher density tetragonal phase barium titanate

using the hydrothermal process, a temperature of above 400°C is required (Kajiyoshi et al. "Preparation of tetragonal barium titanate thin film on titanium metal substrate by hydrothermal method", J. Am. Ceram. Soc., 74, pp 369-74,1991).

5 The cubic-phase and lower density of hydrothermally produced barium titanate can be explained because of the existence of lattice defects such as hydroxyls (OH⁻) in small particles. According to Vivekanandan et al., the OH⁻ included in barium titanate particles prepared hydrothermally contribute to the stabilization of a cubic phase at room temperature which is normally observed only at temperatures above the ferroelectric Curie point at 130°C (Vivekanandan et al, Hydrothermal preparation of
10 Ba(Ti,Zr)O₃ powders, Mater. Res. Bull., 22, pp 99-108, 1986). In a publication by Hennings et al., the authors indicate that tetragonal phase barium titanate is obtained upon heat-treatment above 600°C (Hennings et al., Characterization of hydrothermal barium titanate, J. Eur. Ceram. Soc., 9, pp 41-46, 1992).

In a later publication, Hennings et al. (Defect chemistry and microstructure of
15 hydrothermal barium titanate, J. Am. Ceram. Soc. 84(1), pp179-182, 2001) show that for commercial (Cabot Performance Materials, BT4) and self-prepared cubic barium titanate of initial density 5.65±0.05g.cm⁻³, all OH⁻ are removed upon heat treating above 600°C as showed by thermogravimetric analysis, but only as of 800°C the density starts increasing reaching 5.97g.cm⁻³ at 1000°C. Also in the temperature range
20 20-400°C, there is a large discrepancy between the theoretical density calculated from the lattice parameters (5.93g.cm⁻³) and the pycnometric density (5.65g.cm⁻³). The model involving defects due to the presence of OH⁻ in the structure up to 600°C however explains the pycnometric density. The lower density of hydrothermal barium titanate is also explained in terms of intragranular porosity which can only disappear
25 with a heat-treatment above 800°C.

However heat-treating barium titanate powders to obtain tetragonal phase (~600°C) and a higher density (~1000°C) leads to the common drawbacks of larger particle size, wide particle size distribution and agglomeration.

To be noted that recent work reported that hydrothermal tetragonal barium titanate can be prepared at a temperature as low as 240°C over several days of synthesis however obtaining submicrometer-sized, even millimeter-sized particles (in Xu et al. Tetragonal Nanocrystalline Barium Titanate Powder: Preparation, Characterization and Dielectric Properties, J. Am. Ceram. Soc., 86(1) pp 203-205, 2003.). As reported
5 by Asiaie et al. (in Characterization of submicron particles of tetragonal BaTiO₃, Chem, Mater., 8 pp 226-234, 1996) tetragonal barium titanate was obtained after 14 days of hydrothermal treatment at 240°C. As a consequence of the long ageing time, particle growth to 0.5 µm. was observed. Xu et al. (idem, 2003) have reported the
10 preparation of nanometer sized tetragonal barium titanate using the hydrothermal process for 12 hours in a 30 ml vessel; however the TEM picture shows a wide size distribution. No information about the density of those tetragonal barium titanate powders is reported (above cited Xu et al., Asiaie et al.).

Summary of the Invention

15 In a main aspect, the invention provides a method of producing a mixed oxide powder of perovskite structure ABO₃ or spinel structure A_xB_yO₄ where A and B are metals of valencies suitable to form compounds of the given structures, and where x/y is 0.2, 0.5, 1.25 or 3.5 depending on the metal valences, including solid solutions and doped compounds of said perovskite and spinel structures. The powder to be produced meets
20 up to specific characteristics as follows. It is composed of non agglomerated ultrafine particles whose shape has a given aspect ratio, of high density corresponding to at least 90% of the intrinsic density of a large crystal of the ABO₃ or A_xB_yO₄ compound. All particles are to be smaller than 1 micron and have a particle size distribution width characterized by a span ($d_{v90}-d_{v10}$)/ d_{v50} less than 1, where d_{v90} refers to a value such that
25 90% of the powder volume is made of smaller sizes, d_{v10} refers to a value such that 10% of the powder volume is made of smaller sizes, and d_{v50} refers to the volume median diameter such that 50% of the powder volume is made of smaller sizes. Moreover, the ratio A:B is very close to ideal stoichiometry.

The method according to the invention for producing powder to this specification comprises two main steps:

- 5 (a) a first stage reaction between reactants composed of compounds of selected metals A and B to produce a mixed oxide powder of structure ABO_3 or $A_xB_yO_4$ composed of non-agglomerated ultrafine particles having a shape of said given aspect ratio, of low density corresponding at most to 85% of said intrinsic density, all particles being smaller than 1 micron and having a particle size distribution span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, and wherein the ratio of A:B is to is very close to ideal stoichiometry; followed by
- 10 (b) subjecting the powder produced in step (a) to a second stage hydrothermal post treatment at a temperature less than 400°C to convert the particles of low density to ultrafine particles of increased density corresponding to at least 90% of said intrinsic density while maintaining said given aspect ratio, and maintaining the size of all particles below 1 micron, the particle size distribution span $(d_{v90}-d_{v10})/d_{v50}$ below 1, and
- 15 the ratio of A:B very close to ideal stoichiometry.

The present invention thus provides a two-step process to prepare high-density mixed oxides of perovskite or spinel structure (e.g. tetragonal barium titanate) composed of ultrafine particles in the median size range of for example 0.15 to 0.5 microns with a given aspect ratio (isotropic or non-isotropic in shape), narrow particle size

20 distributions, lack of agglomerates, an A/B ratio very close to the ideal stoichiometry (e.g. Ba/Ti ratio very close to 1) and high purity. This process involves the use of low cost raw materials and does not require either subsequent milling or high temperature thermal treatment.

The span of particle size distribution is maintained or can be decreased from step (a) to

25 step (b), with a shift of the particle size distribution $(d_{v10}, d_{v50}, d_{v90})$ towards higher sizes after the hydrothermal post-treatment of step (b). Thus, the particles may grow during the hydrothermal post-treatment step (b), and may alter shape, however maintaining essentially the same aspect ratio (ratio of their key dimensions). For instance, the growth of isotropic particles may produce a change of shape from say

spherical shape to more cubic shape, however conserving isotropy, whereas anisotropic particles like needle-like particles can grow by sharpening their edges, also maintaining their overall aspect ratio. The hydrothermal post treatment step may also produce a change of the crystal structure of the particles, e.g. from cubic to tetragonal crystal structure in the case of barium titanate.

This process can be applied in particular to the preparation of high density barium titanate or solid solutions of barium titanate or other oxides based on barium and titanium having the general structure $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$, where A represents one or more divalent metals such as calcium, lead, strontium, magnesium and zinc and B represents one or more tetravalent metals such as tin, zirconium and hafnium, as well as to high density doped barium titanate and high density doped solid solutions of barium titanate or other oxides based on barium and titanium having the general structure $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$.

Firstly a low temperature (temperature usually in the range 70°C up to boiling temperature at a pressure of 1 bar) continuous process, which may implement Segmented Flow Tubular Reactor technology according to WO98/02237, is used to prepare ultrafine (e.g. spherical shaped particles of median particle size 0.02 – 0.5 microns) mixed oxide particles, for example low-density cubic barium titanate particles, exhibiting the above-described final characteristics except high density and, for barium titanate, a tetragonal structure. In a Segmented Flow Tubular Reactor (SFTR) reaction volumes, conveniently of up to 100ml, usually less than 20ml, are separated by a segmenting fluid that is not miscible with the reaction mixture, in a tube typically having a diameter of about 2-10 mm. A reaction time of few minutes already is long enough to produce these low density mixed oxide powders such as barium titanate.

Alternatively, step (a) is performed using a discontinuous fed-batch reactor of up to 1 litre reaction volume, or using a continuous mixed suspension-mixed product removal (MSMPR) reactor of up to 1 litre residence volume.

Secondly, a high temperature (temperature usually above 100°C, and preferably in the range 200-350°C) hydrothermal post-treatment is applied to the particles, e.g. cubic barium titanate particles, produced in the first step to transform them into high-density particles exhibiting all the above described final characteristics. For barium titanate, the transformation from cubic low density to high density and tetragonal is achieved in only 6 hours, likewise for most other mixed oxides.

This two-step process allows for the production of commercial quantities of high quality mixed oxide perovskite or spinel particles for specific applications, e.g. barium titanate powders adapted for small size multilayer ceramic capacitors and embedded capacitances requiring the smallest barium titanate particles.

Further features and embodiments of the invention are set out in the claims.

Brief description of the drawings

Fig.1 is an X-ray diffraction pattern of cubic barium titanate obtained Example 1.

Fig. 2 is the volumetric particle size distribution of the barium titanate obtained in Example 1.

Fig. 3 is an SEM micrograph of the spherical-shaped barium titanate obtained in Example 1.

Fig. 4 is the particle size distribution of the barium titanate obtained in Example 4.

Fig. 5 is an SEM micrograph of the barium titanate obtained in Example 4.

Fig. 6 is an X-ray diffraction pattern in the region 2-theta 52 to 54 degrees of tetragonal barium titanate obtained in Example 4.

Fig. 7 is an X-ray diffraction pattern of tetragonal barium titanate obtained in Example 8.

Fig. 8 is the particle size distribution of the barium titanate obtained in Example 8.

Fig. 9 is an SEM micrograph of the barium titanate obtained in Example 8.

Fig. 10 is the particle size distribution of the barium titanate obtained in comparative Example 9.

Fig. 11 is an SEM micrograph of the barium titanate obtained in Example 9.

- 5 Fig. 12 is the particle size distribution of the barium titanate obtained by a comparative post heat treatment in Example 10.

Detailed Description of the Invention

Production of Basic Compounds

10 The present invention provides a two-step process to prepare high-density perovskite and spinel mixed oxides, for instance tetragonal barium titanate powders composed of ultrafine particles in the median size range 0.05 to 0.5 microns with isotropic shape, narrow particle size distributions, lack of agglomerates, a Ba/Ti ratio very close to 1 and high purity. This process involves the use of low cost raw materials and does not require either subsequent milling or high temperature thermal treatment.

- 15 The first step is a low temperature continuous process where either a discontinuous one liter fed-batch reactor; or a continuous mixed suspension-mixed product removal (MSMPR) reactor of one liter residence volume; or any other process generating continuously small reaction volumes, or a Segmented Flow Tubular Reactor (SFTR) as described in WO98/02237, is used to prepare ultrafine low-density cubic barium
20 titanate particles.

A first aqueous solution is prepared using soluble barium and titanium reactants (e.g. BaCl_2 and TiCl_4) with Ba/Ti ratio larger than 1 and titanium concentration in the range about 0.6-0.06 mol/Kg. The Ba/Ti ratio changes as a function of titanium concentration, in the range 1.01-1.2 to lead to a cubic barium titanate product of ideal stoichiometry. A
25 second solution is prepared from a strong base compound (e.g. NaOH). The two solutions are mixed and mechanically homogenized in order to produce a gel. The

strong base compound concentration in the second solution is calculated to obtain pH of about 14 after complete transformation into barium titanate. The as-prepared gel is an amorphous titanium hydroxide network with adsorbed barium ions. The gel is fed to a SFTR and segmented with an immiscible fluid. The SFTR is maintained at the appropriate reaction temperature (in the range 70°C up to boiling temperature at a pressure of 1 bar). The ageing time is typically in the range 2 to 20 minutes. During the ageing time, the gel is transformed into single-phase low-density barium titanate suspension. The suspension is recovered and the powder washed in water until pH is above 11 and then in an NH_4OH solution until chlorine concentration in the supernatant is below 10ppm.

X-Ray Diffraction analysis detects a typical cubic barium titanate pattern without any secondary phases such as barium carbonate, Ba-rich or Ti-rich mixed oxides. The Ba/Ti ratio in the powder has been measured by Inductively Coupled Plasma spectrometry and is equal to 1.00 ± 0.01 . The density measured by helium pycnometry was in the range 5.0-5.1 g.cm⁻³, this value is also consistent with a cubic low-density barium titanate. Thermogravimetric analysis carried out from 25 to 500°C detects a weight loss of about 4 % attributed to the removal of hydroxyls present within the barium titanate structure; this is also consistent with a cubic low-density barium titanate.

Adjusting the synthesis parameters such as the reactant concentration, Ba/Ti ratio in the first solution, the temperature and the gel flow rate allows for fine-tuning the median diameter (d_{v50}) of the barium titanate particles in the range of 0.02 to 0.5 microns. The particle size distribution is measured using a sedimentation technique. The width of the particle size distribution is evaluated by the span, which corresponds to $(d_{v90} - d_{v10})/d_{v50}$. This span is below 1.0, typically about 0.7 (d_{vX} is a particle diameter meaning that X% of the powder volume is made of smaller sizes).

The second step is a high temperature hydrothermal post-treatment applied to the cubic low-density barium titanate particles produced in the first step to transform them into high-density tetragonal barium titanate. The temperature is above 100°C, preferably in the range 200-350°C.

A barium solution at high pH is prepared either from a barium salt and a strong base reactant (e.g. BaCl_2 and NaOH) or using $\text{Ba}(\text{OH})_2$. It is mixed with the cubic barium titanate particles prepared in the first step using the SFTR and the resulting suspension is homogenized. The solid/liquid ratio can be as large as 50% weight. The suspension is transferred to a Teflon coated autoclave and treated at a temperature above 200°C and for times from 2 to 20 hours. The second step can also be carried out in a continuous hydrothermal apparatus. The suspension is recovered and the powder washed in water until pH is above 11 and then in an NH_4OH solution until chlorine concentration in the supernatant is below 10ppm. After washing, the powder is dried.

X-Ray Diffraction analysis detects a typical tetragonal barium titanate pattern without any secondary phases such as barium carbonate, Ba-rich or Ti-rich mixed oxides. The Ba/Ti ratio in the powder has been measured by Inductively Coupled Plasma spectrometry (ICP-AES) and is equal to 1.00 ± 0.01 . The density measured by helium pycnometry is in the range $5.60\text{-}5.75\text{g.cm}^{-3}$. Thermogravimetric analysis carried out from 25 to 500°C detects a weight loss of only 0.80% maximum attributed to the removal of residual hydroxyls present within the barium titanate structure; this value slightly varies upon the post-treatment conditions.

Adjusting the synthesis parameters such as the reactant concentration, Ba/Ti ratio in the first solution, the temperature and the post-treatment time allows for fine-tuning the median diameter (d_{v50}) of the barium titanate particles in the range of 0.05 to 0.5 microns. The particle size distribution is measured using a sedimentation technique. The width of the size distribution is evaluated by the span, which corresponds to $(d_{v90} - d_{v10})/d_{v50}$. This span is in the range 0.4-0.8, depending on the post-treatment parameters.

This hydrothermal post-treatment is necessary to transform the high quality cubic barium titanate prepared in the first step of the process into high quality tetragonal barium titanate while maintaining the other key characteristics obtained through the first step (isotropic, narrow particle size distributions, lack of agglomerates and a Ba/Ti ratio very close to 1). The duration of the hydrothermal post-treatment also allows for

increasing the median particle size (d_{v50}) while ensuring the particle size distribution is narrow. In addition, after performing the hydrothermal post-treatment it has been shown that the powder contains about 10 to 20 times less sodium than before, with a sodium concentration in the range 10 to 35ppm depending on the post-treatment conditions.

Using the barium titanate powder prepared according to the method to prepare a ceramic body allows for determining dielectric properties of such a ceramic body. Cylindrical rods of 8-9.5 mm in diameter are made by isostatic pressing and sintered at different temperatures for a fixed time. Discs approximately 1 mm thick were cut from the rods, flat parallel faces were ground with emery and gold electrodes were evaporated onto them in order to prepare a capacitor. The capacitance and dielectric losses were measured between 30 and 170°C and were satisfactory for commercial applications.

Substitution and doping

The electrical properties of barium titanate can be substantially modified by the incorporation of barium and titanium substituents to form solid solutions and/or as dopants.

Solid solutions of barium titanate or other oxides based on barium and titanium have the general structure $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$, where A represents one or more divalent metals such as calcium, cadmium, europium, magnesium, lead, radium, strontium and zinc and B represents one or more tetravalent metals such as cerium, cobalt, iron, hafnium, molybdenum, lead, praseodymium, plutonium, ruthenium, tin, thorium, titanium, uranium, vanadium and zirconium.

One type of barium titanate-based composition has the structure $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$, where the mole fractions x and y can be in the range of 0 to 1, preferably larger than 0.03, where A represents one or more divalent metal other than barium such as calcium, cadmium, europium, magnesium, lead, radium, strontium and zinc and B represents one or more tetravalent metals other than titanium such as cerium, cobalt, iron, hafnium,

molybdenum, lead, praseodymium, plutonium, ruthenium, tin, thorium, uranium, vanadium and zirconium.

Where the divalent or tetravalent metals are present as dopants, the value of the mole fraction x and y may be small, for example less than 0.1.

- 5 In other cases, the divalent or tetravalent metals may be introduced at higher levels to provide a significantly identifiable compound such as barium-calcium titanate, barium-strontium titanate, barium titanate-zirconate and the like.

- In still other cases, where x or y is 1.0, barium or titanium may be completely replaced by the alternative metal of appropriate valence to provide a compound such as lead titanate or barium zirconate.
- 10

The powder composition also shows a mole ratio of $(Ba+A)/(Ti+B)$ close to 1.00.

- Different cations (e.g. calcium, cadmium, europium, magnesium, lead, radium, zinc, cerium, iron, hafnium, molybdenum, praseodymium, plutonium, ruthenium, tin, thorium, uranium and zirconium e.g. in the form of chlorides but not limited to chlorides), one or more as desired, can substitute the barium (or A) and/or titanium (or B) reactants of the first solution used to prepare the gel before completing the first step of the process. The low density barium titanate-based particles prepared through the first step of the process are then transformed into high density barium titanate-based particles $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ through the above-described hydrothermal post-treatment.
- 15

- 20 Dopants cover a wide range of metal oxides. These, in general but not limited, represent less than 0.05 mole fraction of the total $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ formulation. The dopant or dopants employed may be completely or partially miscible in the perovskite lattice or may be immiscible in the lattice. The dopant is selected from the group consisting of lanthanum, rare earth elements, lithium, magnesium, yttrium, niobium, tantalum, gallium, molybdenum, tungsten, manganese, copper, iron, cobalt, nickel, chromium, zinc, aluminium, silicon, antimony, lead, bismuth, boron and mixtures thereof and is different to A and B.
- 25

It is possible to obtain homogeneously doped low density barium titanate or doped low density $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ compound using a modified procedure of the first step of the process. The desired cations are added in the form of e.g. chlorides to the first aqueous solution containing soluble barium and titanium reactants either before the gel is prepared or after the gel has been prepared and then aged in the SFTR. The doped barium titanate or low density doped $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ compound prepared through the first step of the process is then transformed into high density doped barium titanate or high density doped $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ compound through the above-described hydrothermal post-treatment.

- 10 Another route to prepare heterogeneously doped barium titanate with a concentration gradient decreasing from the particles surface to their core is to use pure low density barium titanate prepared through the first step of the process and modifying the second step of the process by replacing (or adding to) the barium compound in the barium solution by the desired metallic cation(s) to obtain doped high density barium titanate.
- 15 Adjusting the dopant concentration in the alkaline solution allows for either getting a gradient or homogenous distribution of dopant within the particles.

This last route can also be used to prepare doped $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ compound with a concentration gradient decreasing from the particles surface to their core. This route uses low density $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$ compound prepared through the first step of the process and modifying the second step of the process by replacing the barium and/or A compound in the alkaline solution by the desired metallic cation(s) in order to produce high density doped $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$. Adjusting the dopant concentration in the alkaline solution allows for either producing a gradient or homogenous distribution of dopant within the particles.

- 20
- 25 Several post-treatments may be carried out one after the other, each one allowing doping with a single or several dopants.

EXAMPLES

The present invention will be described in more detail hereinunder by Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention thereto.

5 Various properties were measured by the following methods.

10 (a) The shape of the barium titanate particles was determined from micrographs made during scanning electron microscope (SEM, PHILIPS XL-30 FEG) observations. The aspect ratio of a particles can also be determined from micrographs. The aspect ratio corresponds to the ratio between the longest dimension and the shortest dimension of the particle, i.e. the aspect ratio of a rod is bigger than 1, the aspect ratio of a disc or platelet is smaller than 1 while it equals 1 for a sphere. More generally, the aspect ratio is defined as the ratio between the particle axis h and the axis b . In a Cartesian coordinate system, h corresponds to the z direction and b to the x - y direction for symmetric bodies. 15 Oblate spheroids will then have aspect ratios $h/b < 1$ and prolate spheroids will have axial ratios $h/b > 1$.

20 (b) The volumetric particle size distributions of the barium titanate particles were measured by sedimentation (XDC, BI-XDCP Particle Sizer, Brookhaven Instrument Corporation). To prepare a suspension for particle size distribution measurement, 0.5g of dry powder was dispersed in 40 ml of a 0.1wt% polyacrylic acid solution. The suspension was sonicated with an ultrasound horn for 15 minutes. The measurement was carried out at 25°C with a disk speed of 1500 rpm. The particle size distribution is characterized by d_{v10} , d_{v50} , d_{v90} : d_{v10} means that 10% of the powder volume is composed of smaller particle sizes, d_{v50} means that 50% of the powder volume is composed of smaller particle sizes and d_{v90} means that 90% of the powder volume is made of smaller sizes. The width of the distribution is defined by the span $[(d_{v90} - d_{v10}) / d_{v50}]$. The smaller the span, the narrower is the particle size distribution. The percentage of 25

agglomerates bigger than 1 micron was also calculated from the particle size distribution data.

- 5
- (c) The specific surface area value was measured by the BET method using a Gemini Micromeritics apparatus after the powder had been heated for 1 hour at 220°C.
- (d) The densities were measured using helium pycnometry (Micromeritics AccuPyc1330) pycnometry after the powder was heated for minimum 24h at 110°C to make sure all adsorbed water had been eliminated.
- 10
- (e) The Ba/Ti ratio was measured using inductively coupled plasma spectrometry (ICP-AES, Perkin Elmer, Plasma 2000 software) as well as the sodium concentration in the powder.
- 15
- (f) Phase purity was investigated by X-ray diffraction (XRD, Co K_{α} radiation, model PW1710, Philips, Eindhoven, The Netherlands) on as-prepared powders and after calcination for 6 h at 950°C and 1350°C. Phase composition after annealing is very sensitive to the overall Ba/Ti molar ratio of the solid. Formation of secondary phases is already observed by XRD for deviations of ± 1 at.% from the ideal stoichiometry if the diffraction pattern is carefully collected. As to the tetragonality of the barium titanate particles of the present invention, the value of c/a has been calculated, wherein 'a' and 'c' are lattice constants for the respective 'a' and 'c' crystal axes.
- 20
- (g) Thermogravimetric analysis (Mettler TG50 thermobalance) measured in the range 200 to 500°C allowed for determining the amount of hydroxyls contained in the barium titanate structure before and after the hydrothermal post-treatment. The measurements were carried out after the powder was heated for minimum 24h at 110°C to make sure all adsorbed water had been eliminated.
- 25

Example 1 – Production of Powder from First Step of the Process

To prepare 1 kg of cubic barium titanate with a median size (d_{v50}) of 75nm, twelve litres of gel were prepared by mixing 6 litres of a NaOH solution at a concentration of 4.42 mol/kg and 6 litres of BaCl₂ and TiCl₄ solution at a concentration of 0.561 mol/kg and 0.550 mol/kg respectively. The gel was fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time of the gel in the tube was between 3 to 5 minutes, over the 2 minutes required to transform the gel into a suspension of barium titanate nanoparticles at this temperature. The suspension was collected at the outlet of the tube in a vessel maintained at room temperature. The suspension was then allowed to decant for 2 hours and about 10 litres of supernatant were removed from the storage vessel. The powder was washed in several steps and then dried. The powder was then characterized.

As presented in Table 1 and illustrated by Figure 2, the particle size distribution shows d_{v50} of 75nm with a d_{v10} and d_{v90} of 48nm and 116nm respectively. As shown in Figure 1, since no diffraction peaks attributed to substances other than BaTiO₃ were recognized, it was confirmed that the obtained particles consisted of BaTiO₃. The powder is considered as cubic as no peak splitting has been identified and $c/a = 1.000$ (see Table 3). Also Figure 3 shows a SEM micrograph of the spherical-shaped barium titanate particles prepared. The density of this powder is 5.00. The Ba/Ti equals 1.00. The powder also contains 500ppm of sodium inherent to NaOH used in this synthesis route. Finally, thermogravimetric analysis shows a weight loss of 4.2% attributed to the presence of hydroxyls in the barium titanate structure.

Example 2 - Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out by mixing 2g of barium titanate produced according to procedure described in Example 1 with 30g of a Ba(OH)₂ solution. This solution was initially prepared by dissolving 16.7g of Ba(OH)₂ in 1 litre of water. The suspension was placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave

required 1 hour, the autoclave was then allowed to stay at this temperature for 1 hour and then to cool naturally to room temperature. The suspension was recovered and the supernatant was removed. The powder was washed in several steps and then dried. The powder was then characterized.

- 5 As presented in Table 1, the particle size distribution shows d_{v50} of 106nm with a d_{v10} and d_{v90} of 71nm and 151nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.002$ (see Table 3). The density of this powder has increased compared to the Example 1 powder: it is 5.60 (± 0.09). The powder only contains 34ppm of sodium compared to 500ppm of Example
- 10 1. Finally, thermogravimetric analysis shows a weight loss of 0.80 % attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 3 - Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out using the same procedure as Example 2, except the hydrothermal autoclave was maintained at 250°C for 2 hours instead of 1

15 hour. After the powder had been washed in several steps and then dried, it was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 130nm with a d_{v10} and d_{v90} of 85nm and 189nm respectively. As shown in Figure 6, the powder is considered as tetragonal as a peak splitting has been identified and $c/a = 1.006$ (see

20 Table 3). Also Figure 5 shows a SEM micrograph of the barium titanate particles, their shape has now become more cube-like than spherical. The density of this powder is 5.58 (± 0.10). The powder also only contains 26ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 0.70% attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 4 - Hydrothermal Post-treatment

25 The hydrothermal post-treatment was carried out using the same procedure as Example 2, except the hydrothermal autoclave was maintained at 250°C for 6 hours instead of 1

hour. After the powder was washed in several steps and then dried, it was then characterized.

As presented in Table 1 and illustrated by Figure 4, the particle size distribution shows d_{v50} of 187nm with a d_{v10} and d_{v90} of 152nm and 229nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.007$ (see Table 3). The density of this powder has increased compared to the Example 1 powder: it is $5.73 (\pm 0.06)$ and its specific surface area is $11.6\text{m}^2/\text{g}$ (see Table 2). The Ba/Ti equals 1.00. The powder only contains 31ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 0.70% attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 5 – Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out by mixing 2g of barium titanate produced according to procedure described in Example 1 with 30g of a BaCl_2 and NaOH solution. This solution was initially prepared by dissolving 13.66g of BaCl_2 and 5g of NaOH in 1 litre of water. The suspension was placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C . Reaching a temperature of 250°C inside the autoclave required 1 hour, the autoclave was then allowed to stay at this temperature for 6 hours and then to cool naturally to room temperature. The suspension was recovered and the supernatant was removed. The powder was washed in several steps and then dried. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 154nm with a d_{v10} and d_{v90} of 105nm and 217nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.006$ (see Table 3). The density of this powder has increased compared to the Example 1 powder: it is $5.71 (\pm 0.01)$ and its specific surface area is $12.1\text{m}^2/\text{g}$ (see Table 2). The Ba/Ti equals 1.00. The powder only contains 65ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 0.80 % attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 6 – Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out by mixing 2g of barium titanate produced according to procedure described in Example 1 with 30g of a BaCl_2 and NaOH solution at pH14. This solution was initially prepared by dissolving 13.66g of BaCl_2 and 40g of NaOH in 1 litre of water. The suspension was placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C . Reaching a temperature of 250°C inside the autoclave required 1 hour, the autoclave was then allowed to stay at this temperature for 6 hours and then to cool naturally to room temperature. The suspension was recovered and the supernatant is removed. The powder was washed in several steps and then dried. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 176nm with a d_{v10} and d_{v90} of 113nm and 248nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.006$ (see Table 3). The density of this powder has increased compared to the Example 1 powder: it is 5.67 (± 0.05) and its specific surface area is $10.5 \text{ m}^2/\text{g}$ (see Table 2). The Ba/Ti ratio equals 1.00. The powder only contains 106ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 0.72% attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 7 – Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out by mixing 2g of barium titanate produced according to procedure described in Example 1 with 30g of a BaCl_2 and NaOH solution at pH14. This solution was initially prepared by dissolving 13.6g of BaCl_2 and 66g of NaOH in 1 litre of water. The suspension was placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C . Reaching a temperature of 250°C inside the autoclave required 1 hour, the autoclave was then allowed to stay at this temperature for 2 hours and then to cool naturally to room temperature. The suspension was recovered and the supernatant was removed. The

powder was washed in several steps and then dried. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 155nm with a d_{v10} and d_{v90} of 117nm and 205nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.002$ (see Table 3). The density of this powder has increased compared to the Example 1 powder: it is already 5.65 (± 0.01) after only 2 hours of post-treatment at 250°C and its specific surface area is 11.3 m²/g (see Table 2). The Ba/Ti ratio equals 1.00. The powder only contains 228ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 1.00 % attributed to the presence of residual hydroxyls in the barium titanate structure.

Example 8 – Hydrothermal Post-treatment

The hydrothermal post-treatment was carried out using the same procedure as Example 7 except the hydrothermal autoclave was maintained at 250°C for 6 hours instead of 2 hours. The suspension was recovered and the supernatant was removed. The powder was washed with several liquids and then dried. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 214nm with a d_{v10} and d_{v90} of 147nm and 297nm respectively. The powder is not considered as cubic as an X-Ray diffraction peak splitting has been identified and $c/a = 1.005$ (see Table 3). The density of this powder has increased compared to the Example 1 powder, it is 5.668 (± 0.005) and its specific surface area is 10.2m²/g (see Table 2). The Ba/Ti equals 1.00. The powder only contains 104ppm of sodium compared to 500ppm of Example 1. Finally, thermogravimetric analysis shows a weight loss of 0.67 % attributed to the presence of residual hydroxyls in the barium titanate structure.

Comparative Example 9 – Production of Powder in One Step

Instead of being fed to the SFTR, 30ml of gel prepared according to the procedure of Example 1 was placed in a 40 ml hydrothermal autoclave, itself placed in an oven

heated at 250°C. Reaching a temperature of 250°C inside the autoclave required 1 hour, the autoclave was then allowed to stay at this temperature for 19 hours and then to cool naturally to room temperature. The suspension was recovered and the supernatant was removed. The powder was washed in several steps and then dried. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 594nm with a d_{v10} and d_{v90} of 248nm and 919nm respectively. The c/a ratio could not be calculated as the XRD peak was too difficult to fit accurately due to the wide particle size distribution. The density is 5.871 (± 0.002). The Ba/Ti equals 1.00. The powder contains 71ppm of sodium. Finally, thermogravimetric analysis shows a weight loss of 0.10 % attributed to the presence of hydroxyls in the barium titanate structure. Despite its high density, this powder shows a much wider particle size distribution than the powders produced using our 2-step process as well as 6% of particles larger than 1 μ m.

Comparative Example 10 – Post Heat Treatment

Two grams of barium titanate produced according to the procedure described in Example 1 were treated for 1 hour in a pre-heated furnace at 600°C. The powder was then characterized.

As presented in Table 1, the particle size distribution shows d_{v50} of 112nm with a d_{v10} and d_{v90} of 57nm and 1068nm respectively with 13 % of particles larger than 1 μ m. The density is only 5.22 (± 0.01) and the specific surface area is 4.7m²/g (see Table 2). Thermogravimetric analysis shows a weight loss of 0.45% attributed to the presence of residual hydroxyls in the barium titanate structure. Despite the low weight loss attributed to the residual hydroxyls, this particle size distribution of this powder shows 13% of particles larger than 1 μ m.

Example 11– Ceramic Body

The barium titanate powder prepared according to the method of Example 1 followed by Example 4 was used to prepare a ceramic body. The powder was used to make

cylindrical rods 8-9.5mm in diameter by isostatic pressing at pressures between 1.15 - 108 and 1.5 -108Pa. These rods were sintered at different temperatures for a fixed time. Discs approximately 1mm thick were cut from the rods, flat parallel faces were ground with emery and gold electrodes were evaporated onto them. The resulting capacitor has satisfactory properties.

5

Table I

Examples	d_{v10} (nm)	d_{v50} (nm)	d_{v90} (nm)	Span	<u>% >1μm</u>
Example 1	48	75	116	0.91	<u>0</u>
Example 2	71	106	151	0.75	<u>0</u>
Example 3	85	130	189	0.80	<u>0</u>
Example 4	152	187	229	0.40	<u>0</u>
Example 5	105	154	217	0.73	<u>0</u>
Example 6	113	176	248	0.77	<u>0</u>
Example 7	117	155	205	0.57	<u>0</u>
Example 8	147	214	297	0.70	<u>0</u>
Example 9	248	594	919	1.13	<u>6</u>
Example 10	57	112	1068	9.00	<u>13</u>

Table 2

Examples	Density (g.cm ⁻³)	Specific surface area (m ² .g ⁻¹)
Example 1	5.0	-
Example 2	5.60 (±0.09)	-
Example 3	5.58 (±0.10)	-
Example 4	5.73 (±0.06)	11.6
Example 5	5.71 (±0.01)	12.1
Example 6	5.67 (±0.05)	10.5
Example 7	5.65 (±0.01)	11.3
Example 8	5.668 ((±0.005)	10.2
Example 9	5.871 (±0.002)	4.7
Example 10	5.22 (±0.01)	-

Table 3

Examples	TGA	XRD	Na (ppm)
	Wt %	c/a	
Example 1	4.2	1.00	500
Example 2	0.8	1.002	34
Example 3	0.7	1.006	26
Example 4	0.7	1.007	31
Example 5	0.8	1.006	65
Example 6	0.72	1.006	106
Example 7	1	1.002	228
Example 8	0.67	1.005	104
Example 9	0.1	•	71
Example 10	0.45	-	-

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- The c/a ratio was not calculated: the XRD peak was too difficult to fit accurately due to the wide particle size distribution.

EXAMPLES OF SPINEL MIXED OXIDES

Example 12 – Production of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ powder

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In the first stage the preparation of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ particles is carried out from a solution containing TiCl_4 at a concentration of 1.0 mol/L and LiOH at a concentration of 1.0 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 15 minutes. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps and then dried. In the second stage $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ powder with 30 ml of a 0.1

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mol/L LiOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 13 – Production of LiMn_2O_4 powder

10 In the first stage the preparation of LiMn_2O_4 particles is carried out from a solution containing a manganate salt i.e. manganese nitrate at a concentration of 0.10 mol/L and LiOH at a concentration of 1.0 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant for 2 hours then the supernatant is removed from the storage vessel. The powder is washed in several steps and then dried. In the second stage LiMn_2O_4 particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of LiMn_2O_4 powder with 30 ml of a 0.1 mol/L LiOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 14 – Production of ZnFe_2O_4 powder

In the first stage the preparation of ZnFe_2O_4 particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, zinc chloride at a concentration of 0.6 mol/L and NaOH at a concentration of 0.5 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then dried. In the second stage ZnFe_2O_4 particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of ZnFe_2O_4 powder with 30ml of a 0.1mol/L NaOH solution. The suspension is placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 15 – Production of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ powder

In the first stage the preparation of $\text{Co}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$ particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, zinc chloride at a concentration of 0.45 mol/L, cobalt chloride at a concentration of 0.2 mol/L and NaOH at a concentration of 0.5 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then dried. In the second stage $\text{Co}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$

particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of $\text{Co}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$ powder with 30 ml of a 0.1 mol/L NaOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 16 – Production of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ powder

In the first stage the preparation of $\text{Ni}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$ particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, zinc chloride at a concentration of 0.45 mol/L, nickel chloride at a concentration of 0.2 mol/L and NaOH at a concentration of 0.5 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then dried. In the second stage $\text{Ni}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$ particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of $\text{Ni}_{0.30}\text{Zn}_{0.70}\text{Fe}_2\text{O}_4$ powder with 30 ml of a 0.1 mol/L NaOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 17 – Production of $Mn_{1-x}Zn_xFe_2O_4$ powder

In the first stage the preparation of $Mn_{0.65}Zn_{0.35}Fe_2O_4$ particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, zinc chloride at a concentration of 0.2 mol/L, manganese chloride at a concentration of 0.33 mol/L and NaOH at a concentration of 0.5 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then dried. In the second stage $Mn_{0.65}Zn_{0.35}Fe_2O_4$ particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ powder with 30 ml of a 0.1 mol/L NaOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 18 – Production of $CoFe_2O_4$ powder

In the first stage the preparation of $CoFe_2O_4$ particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, cobalt chloride at a concentration of 0.5 mol/L and NaOH at a concentration of 1 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then

dried. In the second stage CoFe_2O_4 particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of CoFe_2O_4 powder with 30ml of a 0.1mol/L NaOH solution. The suspension is placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C . Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 19 – Production of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ powder

In the first stage the preparation of $\text{Ni}_{0.30}\text{Co}_{0.70}\text{Fe}_2\text{O}_4$ particles is carried out from a solution containing iron chloride at a concentration of 1.0 mol/L, cobalt chloride at a concentration of 0.35 mol/L, nickel chloride at a concentration of 0.15 mol/L and NaOH at a concentration of 1.0 mol/L. The solution is fed to a Segmented Flow Tubular Reactor comprising a tube is immersed in a water bath maintained at 98°C . The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then dried. In the second stage $\text{Ni}_{0.30}\text{Co}_{0.70}\text{Fe}_2\text{O}_4$ particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of $\text{Ni}_{0.30}\text{Co}_{0.70}\text{Fe}_2\text{O}_4$ powder with 30 ml of a 0.1 mol/L NaOH solution. The suspension is placed in a 40 ml hydrothermal autoclave, itself placed in an oven heated at 250°C . Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.

Example 20 – Production of ZnGa_2O_4 powder

- In the first stage the preparation of ZnGa_2O_4 particles is carried out from a solution containing gallium sulfate at a concentration of 1.0 mol/L, zinc sulfate at a concentration of 0.6 mol/L and NaOH at a concentration of 0.5 mol/L. The solution is
- 5 fed to a Segmented Flow Tubular Reactor comprising a tube immersed in a water bath maintained at 98°C. The residence time in the tube is about 1 hour. The suspension is collected at the outlet of the tube in a vessel maintained at room temperature. The suspension is then allowed to decant then the supernatant is removed from the storage vessel. The powder is washed in several steps to remove the chloride ions and then
- 10 dried. In the second stage ZnGa_2O_4 particles are then subjected to a hydrothermal post-treatment that is carried out by mixing 2g of ZnGa_2O_4 powder with 30ml of a 0.1mol/L NaOH solution. The suspension is placed in a 40ml hydrothermal autoclave, itself placed in an oven heated at 250°C. Reaching a temperature of 250°C inside the autoclave requires about 1 hour, the autoclave is then allowed to stay at this
- 15 temperature for at least 1 hour and up to 6 hours to allow the density of the powder to reach at least 90% of intrinsic density of a large crystal. However, while the particles grow, the other characteristics of the powder are maintained. The autoclave is then cooled naturally to room temperature. The suspension is recovered and the supernatant is removed. The powder is washed in several steps and then dried.
- 20 All of the Examples above are described on laboratory scale. To scale up for industrial production, the powder of the first step of the process can be prepared in an SFTR apparatus with multiple reaction tubes, however while maintaining suitable small segmented reaction volumes. On the other hand, the hydrothermal post treatment can be scaled up by increasing the size of the reactor/autoclave or by using a continuous
- 25 hydrothermal apparatus.

Other Perovskites and Spinels

The invention has been particularly described above by way of example in relation to powders of barium titanate, barium titanate solid solutions and doped barium titanate

and various spinels. Generally the invention applies to other mixed oxides of perovskite or spinel structure.

In the perovskite structure ABO_3 , the A cation is coordinated with twelve oxygen ions and the B cation with six. Thus the A cation is normally found to be somewhat larger than the B cation. In the perovskite structure $A(B'_x B''_y)O_3$, with $x+y=1$ the B' and B'' elements share the positions occupied by the B elements in the perovskite structure ABO_3 . The method according to the invention can be applied to the following types of perovskites.

Ternary ABO_3 type and their solid solutions:

- 10 - ABO_3 where at least one monovalent metal A is in combination with at least one pentavalent metal B,
- ABO_3 where at least one divalent metal A is in combination with at least one tetravalent metal B,
- ABO_3 where at least one trivalent metal A is in combination with at least one trivalent metal B.

Complex oxides: $A(B'_x B''_y)O_3$ type compound where $x+y=1$:

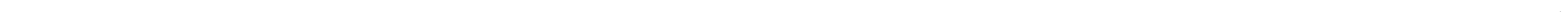
- $A(B'_{2/3} B''_{1/3})O_3$ where at least one divalent metal A is in combination with at least one trivalent metal B' and at least one hexavalent metal B'' ,
- $A(B'_{1/3} B''_{2/3})O_3$ where at least one divalent metal A is in combination with at least one divalent metal B' and at least one pentavalent metal B'' ,
- $A(B'_{1/2} B''_{1/2})O_3$ where at least one divalent metal A is in combination with at least one trivalent metal B' and at least one pentavalent metal B'' ,
- $A(B'_{1/2} B''_{1/2})O_3$ where at least one divalent metal A is in combination with at least one divalent metal B' and at least one hexavalent metal B'' ,
- 25 - $A(B'_{1/2} B''_{1/2})O_3$ where at least one trivalent metal A is in combination with at least one divalent metal B' and at least one tetravalent metal B'' .

The spinel group of minerals has a general composition $A_xB_yO_4$ and is named after the mineral spinel $MgAl_2O_4$. The spinel structure is usually described as a cubic close-packed array of oxygen atoms with the A and B cations occupying one eighth of the tetrahedral sites and one half of the octahedral sites.

- 5 A characteristic of the spinel structure is its flexibility in the range of cations and cation charge combination it will accept, making it a structure adopted by over a hundred compounds, many of them important mineral or important commercial magnetic oxides.
- 10 Principal commercial applications of the spinels are catalysts, magnetic materials and semiconductors. Lithium based spinels such as $LiMn_2O_4$ or $Li_{4/3}Ti_{5/3}O_4$ are attractive cathode materials for rechargeable batteries. The manganese zinc ferrites spinels $Mn_{1-x}Zn_xFe_2O_4$ ($0 < x < 1$) are extensively applied in power transformer, choke coil, noise filter and other electronic components such as multilayer chip and LC filter, read/write heads for high speed magnetic recording, due to their high initial permeability, high
- 15 saturation magnetization and low magnetic loss at high frequency. $ZnGa_2O_4$ is a transparent and conductive material having various applications, such as transparent electrodes in liquid crystal displays and solar cells, because of its optical transparency and metallic conductivity. It has also attracted interest as a good low-voltage phosphor material.
- 20 The method according to the invention can be applied to the following types of spinels.
 - $A_{1/2}B_{5/2}O_4$ where at least one monovalent metal A is in combination with at least one trivalent metal B,
 - $A_{4/3}B_{5/3}O_4$ where at least one monovalent metal A in combination with at least one tetravalent metal B. An example of such a compound is $Li_{4/3}Ti_{5/3}O_4$,
 - 25 - $A_{7/3}B_{2/3}O_4$ where at least one divalent metal A is in combination with at least one pentavalent metal B,
 - AB_2O_4 where A is a monovalent metal (lithium) is in combination with at least one metal B of mixed valences 3 and 4 where B can be partially substituted by iron,

nickel, gallium, aluminum, chromium, copper, cobalt, manganese, zinc and mixtures thereof. An example of such a compound is LiMn_2O_4 ,

- AB_2O_4 where at least one divalent metal A is in combination with at least one trivalent metal B. Examples of such compounds are ZnFe_2O_4 , $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, CoFe_2O_4 , $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$, ZnGa_2O_4 ,
- AB_2O_4 : where at least one tetravalent metal A is in combination with at least one divalent metal B.



CLAIMS

1. A method of producing a mixed oxide powder of perovskite structure ABO_3 or spinel structure $A_xB_yO_4$ where A and B are metals of valencies suitable to form compounds of the given structures, and where x/y is 0.2, 0.5, 1.25 or 3.5 depending on the metal valences, including solid solutions and doped compounds of said perovskite and spinel structures, which powder is composed of non agglomerated ultrafine particles having a shape of given aspect ratio, of high density corresponding to at least 90% of the intrinsic density of a large crystal of the ABO_3 or $A_xB_yO_4$ compound, all particles being smaller than 1 micron and having a particle size distribution width characterized by a span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, where d_{v90} refers to a value such that 90% of the powder volume is made of smaller sizes, d_{v10} refers to a value such that 10% of the powder volume is made of smaller sizes, and d_{v50} refers to the volume median diameter such that 50% of the powder volume is made of smaller sizes, and wherein the ratio A:B is very close to ideal stoichiometry, the method comprising:
 - (a) carrying out a first stage reaction between reactants composed of compounds of selected metals A and B to produce a mixed oxide powder of structure ABO_3 or $A_xB_yO_4$ composed of non-agglomerated ultrafine particles having a shape of said given aspect ratio, of low density corresponding at most to 85% of said intrinsic density, all particles being smaller than 1 micron and having a particle size distribution span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, and wherein the ratio of A:B is very close to ideal stoichiometry; and
 - (b) subjecting the powder produced in step (a) to a second stage hydrothermal post treatment at a temperature less than 400°C to convert the particles of low density to ultrafine particles of increased density corresponding to at least 90% of said intrinsic density while maintaining said given aspect ratio, and maintaining the size of all particles below 1 micron, the particle size

distribution span $(d_{v90}-d_{v10})/d_{v50}$ below 1, and the ratio of A:B very close to ideal stoichiometry.

2. The method of claim 1, wherein the produced mixed oxide powder is of perovskite structure ABO_3 comprising at least one monovalent metal A in combination with at least one pentavalent metal B, or at least one divalent metal A in combination with at least one tetravalent metal B, or at least one trivalent metal A in combination with at least one trivalent metal B ; or is of perovskite structure $A(B'_x B''_y)O_3$ (where $x + y = 1$) comprising either at least one divalent metal A in combination with at least one trivalent metal B' and at least one hexavalent metal B'' (where $x = 2/3$ and $y = 1/3$), or at least one divalent metal A in combination with at least one divalent metal B' and at least one pentavalent metal B'' (where $x = 1/3$ and $y = 2/3$), or at least one divalent metal A in combination with at least one trivalent metal B' and at least one pentavalent metal B'' (where $x = 1/2$ and $y = 1/2$), or at least one divalent metal A in combination with at least one divalent metal B' and at least one hexavalent metal B'' (where $x = 1/2$ and $y = 1/2$), or at least one trivalent metal A in combination with at least one divalent metal B' and at least one tetravalent metal B'' (where $x = 1/2$ and $y = 1/2$) .
3. The method of claim 2, wherein the produced mixed oxide powder is of perovskite structure ABO_3 comprising at least one divalent metal A selected from barium, calcium, cadmium, europium, magnesium, lead, radium, strontium and zinc and least one tetravalent metal B selected from cerium, cobalt, iron, hafnium, molybdenum, lead, praseodymium, plutonium, ruthenium, tin, thorium, titanium, uranium, vanadium and zirconium.
4. The method of claim 3, wherein the produced mixed oxide is $BaTiO_3$, or a solid solution of composition $Ba_{(1-x)}A_xTi_{(1-y)}B_yO_3$, where the mole fractions x and y are each in the range between 0 and 1, preferably larger than 0.03.

5. The method of claim 4, wherein the produced mixed oxide powder is a doped solid solution of composition $Ba_{(1-x-a)}A_xX_aTi_{(1-y-b)}B_yY_bO_3$, where the mole fractions x and y are in the range of 0 to 1, preferably larger than 0.03, the mole fractions a and b are in the range 0 to 0.2, preferably below 0.05, A represents one or more of said divalent metals other than barium, B represents one or more of said tetravalent metals other than titanium, and X and Y each represent one or more other metals selected from the group consisting of lanthanum, rare earth elements, lithium, magnesium, yttrium, niobium, tantalum, gallium, molybdenum, tungsten, manganese, copper, iron, cobalt, nickel, chromium, zinc, aluminium, silicon, antimony, lead, bismuth, boron and mixtures thereof.
6. The method of claim 4, wherein the produced mixed oxide powder is a doped barium titanate $Ba_{(1-a)}X_aTi_{(1-b)}Y_bO_3$, where the mole fractions a and b are in the range between 0 to 0.2, preferably below 0.05, and X and Y each represent one or more metals selected from the group consisting of lanthanum, rare earth elements, lithium, magnesium, yttrium, niobium, tantalum, gallium, molybdenum, tungsten, manganese, copper, iron, cobalt, nickel, chromium, zinc, aluminium, silicon, antimony, lead, bismuth, boron and mixtures thereof.
7. The method of claim 5 or 6, wherein the dopant elements X and/or Y are introduced as reagents in step (a) to ensure homogeneous dopant distribution within the structure, and/or as reagents in step (b) to ensure a gradient of dopant concentration from the particle surface to the particle core.
8. The method of claim 1, wherein the produced mixed oxide powder is of spinel structure $A_xB_yO_4$ comprising: at least one monovalent metal A in combination with at least one trivalent metal B (where $x = 1/2$ and $y = 5/2$); or at least one monovalent metal A in combination with at least one tetravalent metal B (where $x = 4/3$ and $y = 5/3$); or at least one monovalent metal A in combination with at least one metal B of mixed valences 3 and 4 (where $x = 1$ and $y = 2$); or at least one divalent metal A in combination with at least one trivalent metal B (where $x = 1$ and $y = 2$); or at least one divalent metal A in combination with at least one

pentavalent metal B (where $x = 7/3$ and $y = 2/3$); or at least one tetravalent metal A in combination with at least one divalent metal B (where $x = 1$ and $y = 2$).

- 5 9. The method of any one of claims 1 to 8, wherein step (a) is performed by preparing a gel at room temperature in particular by mixing a mixture of salts or hydroxides of metal(s) A and metal(s) B with NaOH or KOH, and subjecting the gel to temperatures in the range 70°C to boiling temperature at a pressure of 1 bar, preferably above 85°C, for a reaction period of 2 to 20 minutes.
- 10 10. The method of claim 9 when depending on claim 7, wherein dopant reagent(s) is/are introduced to the gel in the form of salts or hydroxides of the dopant elements to produce the doped solid solution.
11. The method of any preceding claim, wherein step (a) is performed using a continuous reactor or a reactor that discontinuously processes reaction volumes of up to 1 litre.
- 15 12. The method of claim 11, wherein step (a) is performed using a discontinuous fed-batch reactor of up to 1 litre reaction volume, or using a continuous mixed suspension-mixed product removal (MSMPR) reactor of up to 1 litre residence volume.
- 20 13. The method of claim 11, wherein step (a) is performed using a Segmented Flow Tubular Reactor wherein reaction volumes are separated by a segmenting fluid that is not miscible with the reaction mixture.
- 25 14. The method of any preceding claim, wherein step (b) is performed by adding the mixed oxide powder produced in step (a) to an aqueous solution of hydroxides of metal(s) A or to an aqueous solution of salts of divalent metal(s) A and of an alkali to produce a suspension, and subjecting the suspension to a hydrothermal post treatment at a pressure above 1 bar and a temperature between 100°C and 400°C, preferably in the range 200-350°C, for a residence period of 2 to 20 hours.

15. The method of any preceding claim, wherein step (b) is performed using a hydrothermal apparatus.
16. The method of any preceding claim, wherein the span of particle size distribution is maintained or decreased from step (a) to step (b), with a shift of the particle size distribution (d_{v10} , d_{v50} , d_{v90}) towards higher sizes after the hydrothermal post-treatment of step (b).
17. A mixed oxide powder of perovskite structure ABO_3 or spinel structure $A_xB_yO_4$ where A and B are metals of valencies suitable to form compounds of the given structures, and where x/y is 0.2, 0.5, 1.25 or 3.5 depending on the metal valences, including solid solutions and doped compounds of said perovskite and spinel structures, obtainable by the method of any preceding claim, consisting of:
 - a. non agglomerated ultrafine particles, all particles being smaller than 1 micron; and having:
 - b. a particle size distribution with d_{v50} in the range 0.05 to 0.5 micron, and a span $(d_{v90}-d_{v10})/d_{v50}$ in the range 0.4 to 0.8;
 - c. a density of at least 90% of said intrinsic density;
 - d. a ratio A/B, or a ratio of the sum of A/B metals, equal to ideal stoichiometry plus or minus 1 atomic percent.
 - e. an isotropic particle shape.
18. The powder of claim 17 which is barium titanate $BaTiO_3$ or a solid solution or doped compound based on barium titanate, the powder exhibiting a tetragonal structure.
19. A method of producing a body, in particular a ceramic body, comprising producing mixed oxide powder of structure ABO_3 or AB_2O_4 by the method of any one of claims 1 to 16, and forming the powder into a body with or without binding agents, in particular by the application of pressure and heat separately or together.

20. The method of claim 19 wherein the powder is barium titanate BaTiO_3 or a solid solution or doped compound based on barium titanate, and the body is a capacitor, formed in particular by the application of pressure and at a temperature above 1000°C .

PROCESS FOR PRODUCING ULTRAFINE MIXED OXIDE POWDERS

ABSTRACT

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A mixed oxide powder of perovskite structure ABO_3 such as $BaTiO_3$ or spinel structure $A_xB_yO_4$, including solid solutions and doped compounds that meets up to specific characteristics is produced by method comprising two main steps. The first step is a
10 reaction, typically in a Segmented Flow Tubular Reactor, between reactants composed of compounds of selected metals A and B to produce a mixed oxide powder of structure ABO_3 or $A_xB_yO_4$ composed of non-agglomerated ultrafine particles having a shape of given aspect ratio, of low density corresponding at most to 85% of the intrinsic density, all particles being smaller than 1 micron and having a narrow particle size distribution
15 and wherein the ratio of A:B is very close to the ideal stoichiometry. This is followed by subjecting the powder produced in the first step to a second stage hydrothermal post treatment typically in a hydrothermal autoclave at a temperature less than 400°C to convert the particles of low density to ultrafine particles of increased density corresponding to at least 90% of the intrinsic density while maintaining the same aspect
20 ratio, and maintaining the size of all particles below 1 micron, the narrow particle size distribution span, and the given ratio of A:B.

FIGURE 1

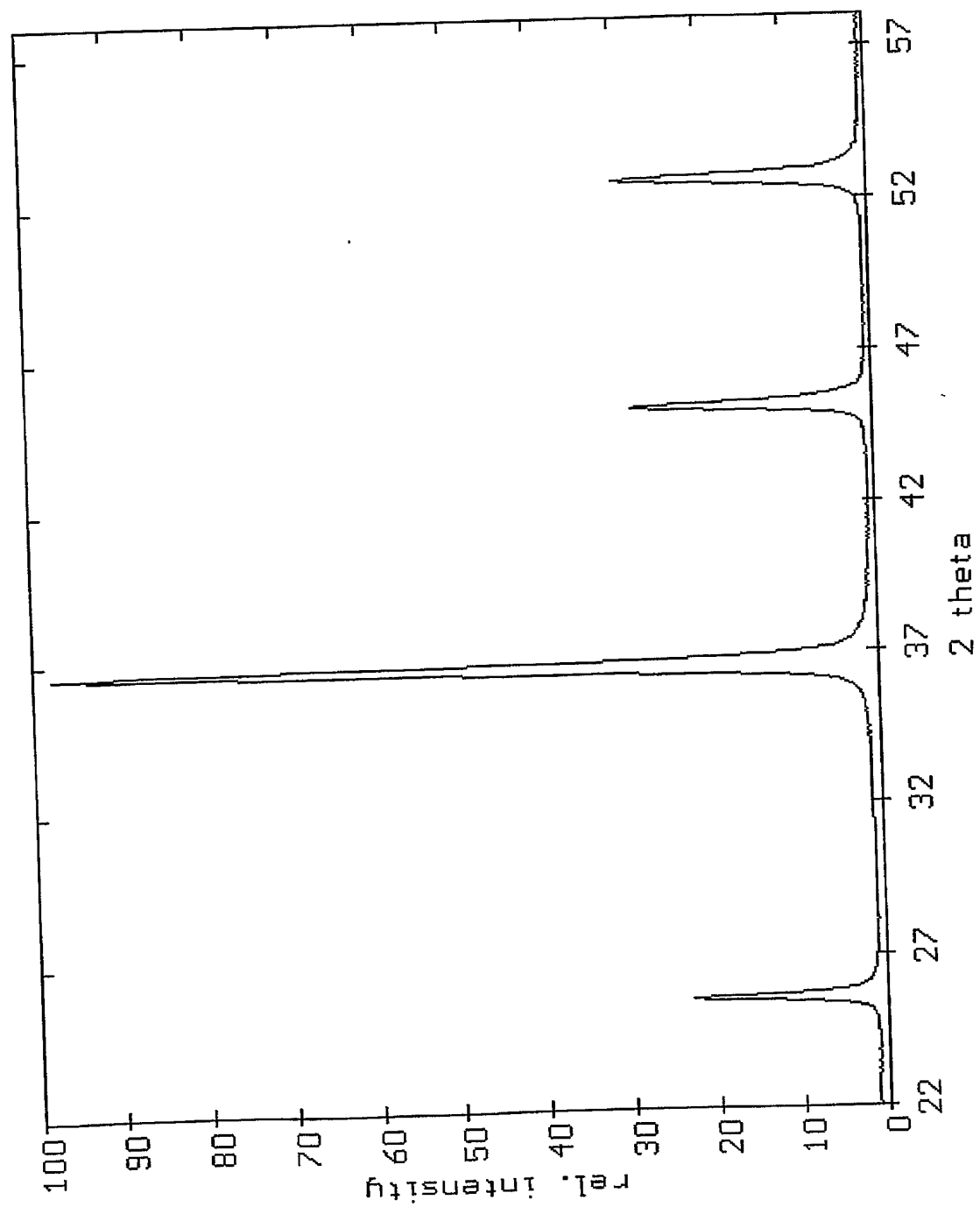


FIGURE 2

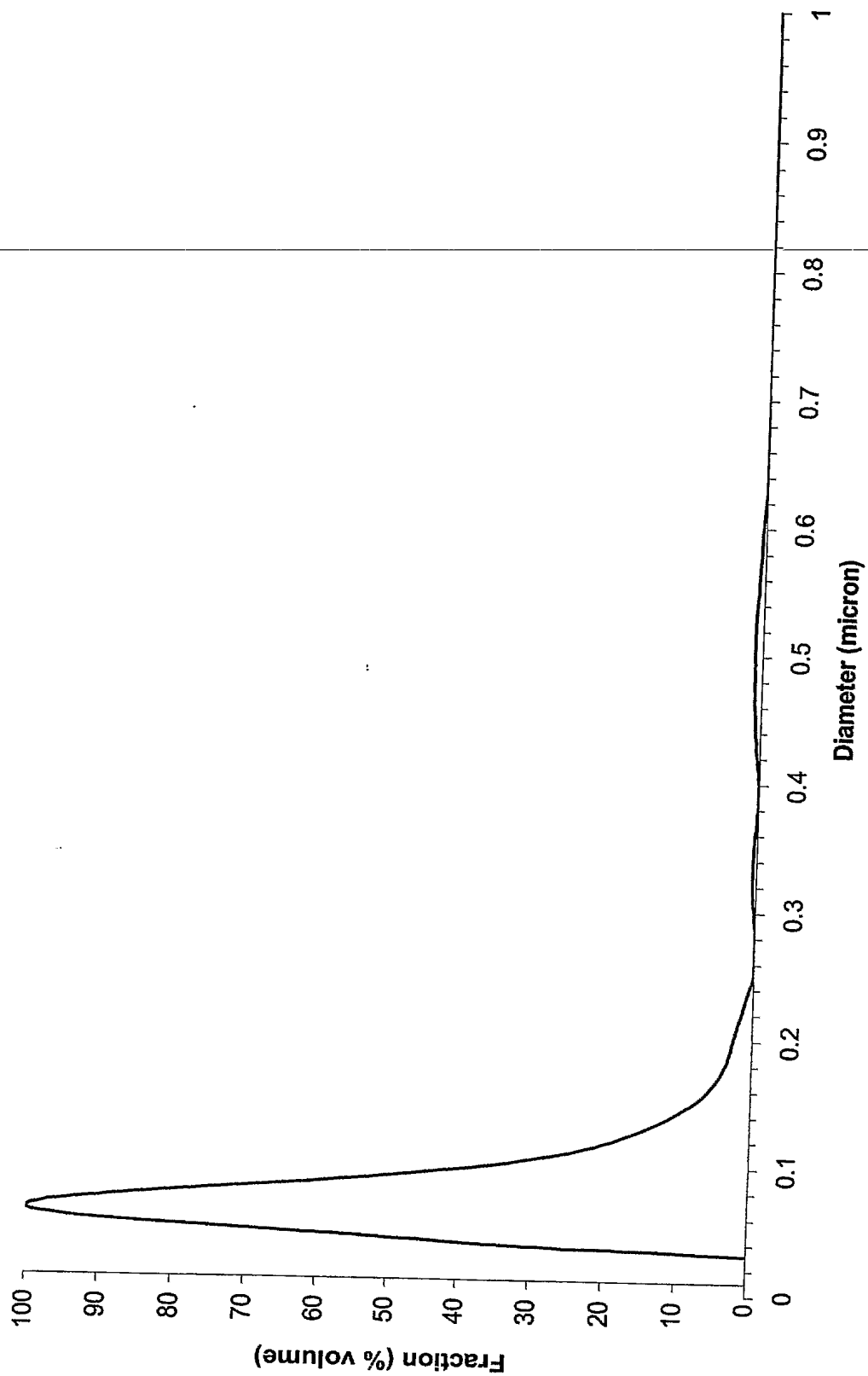


FIGURE 3

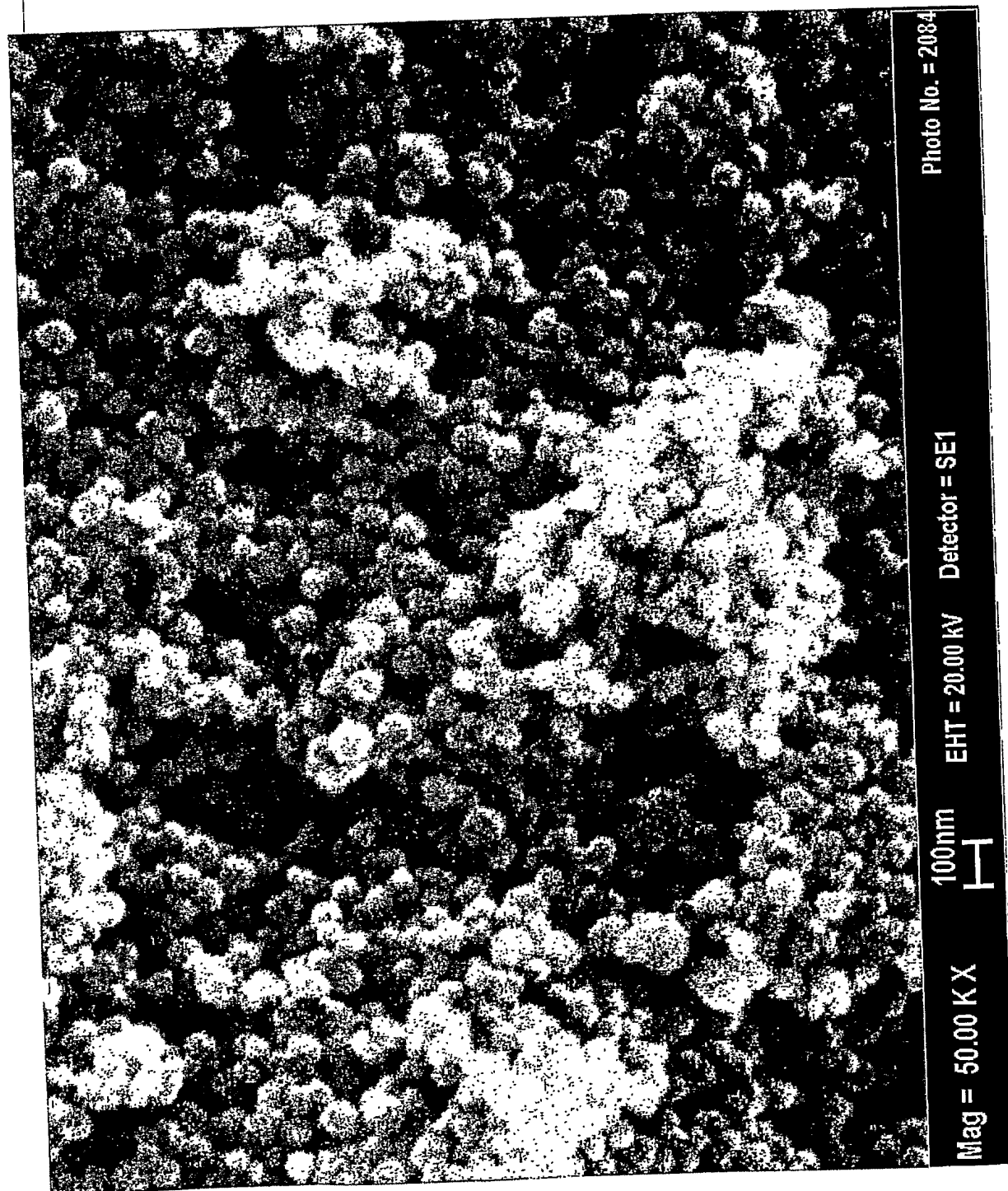


FIGURE 4

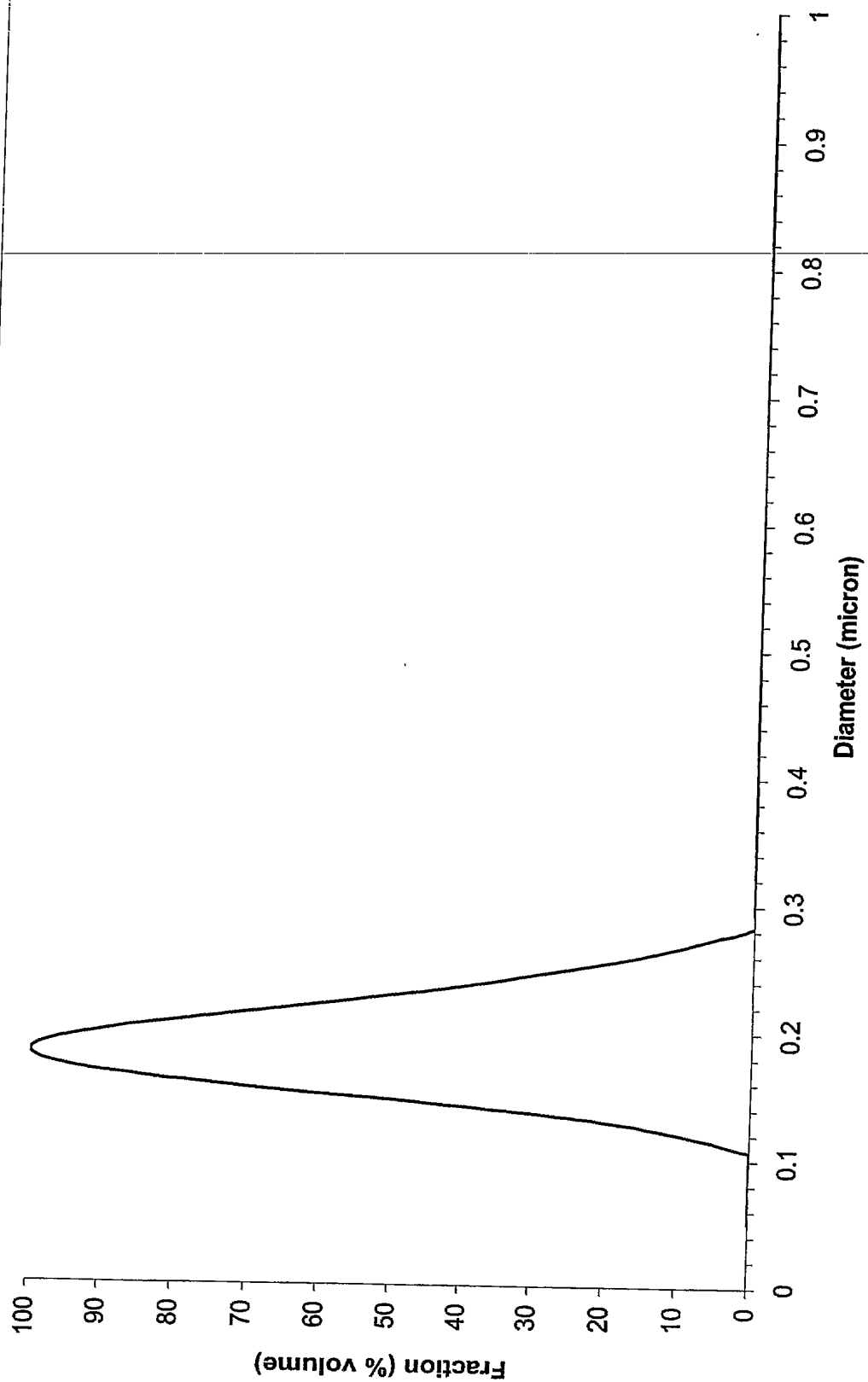


FIGURE 5

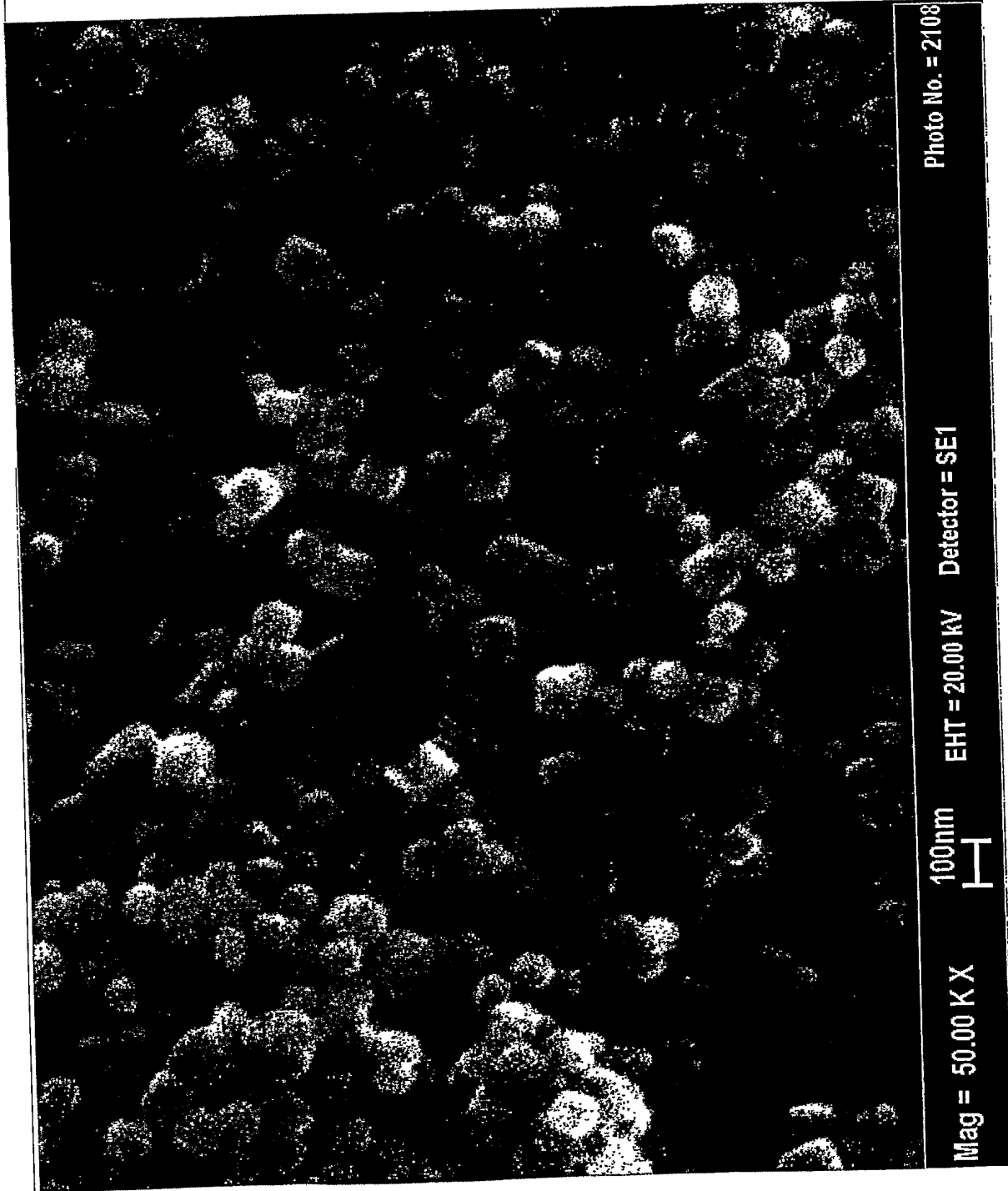


FIGURE 6

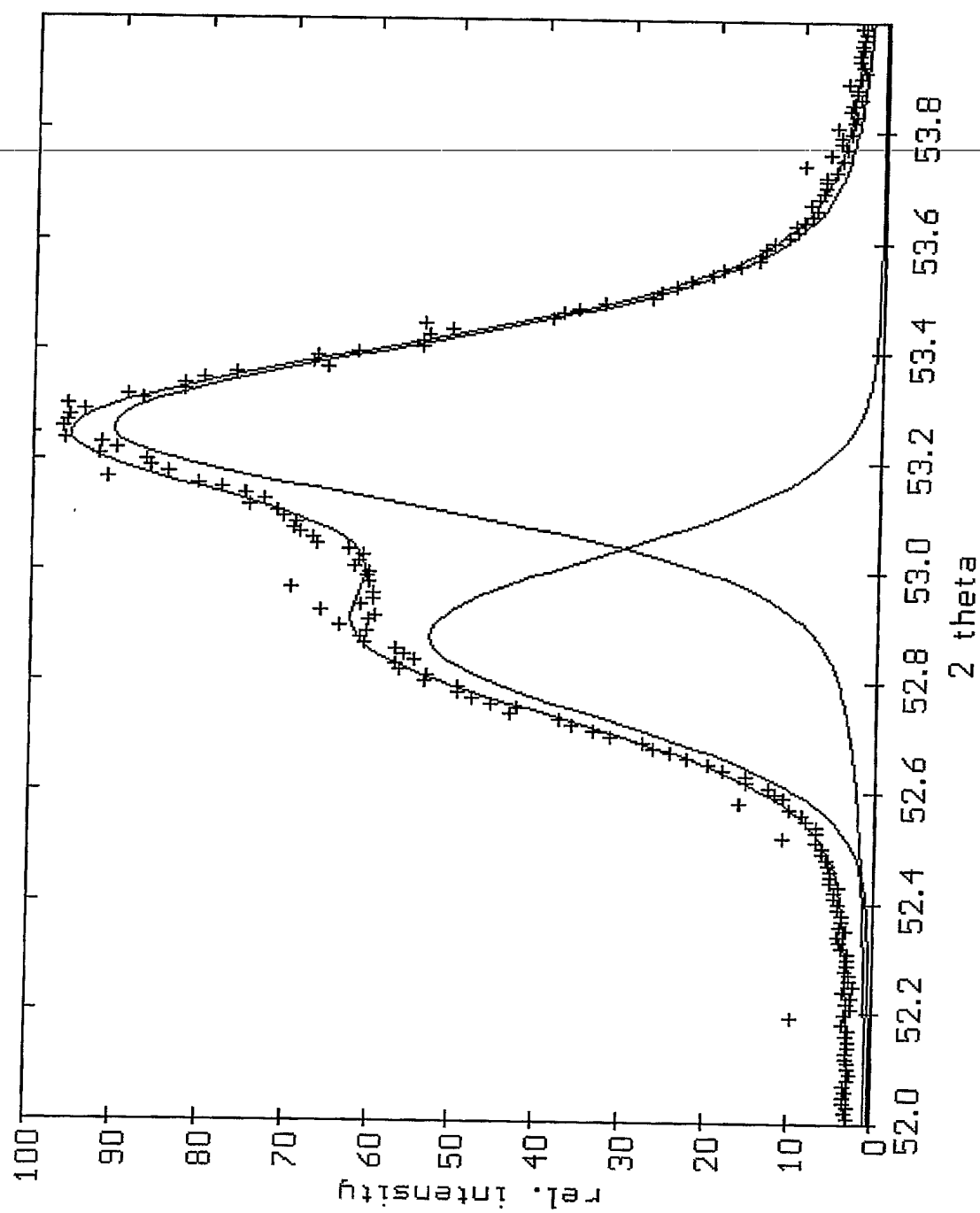


FIGURE 7

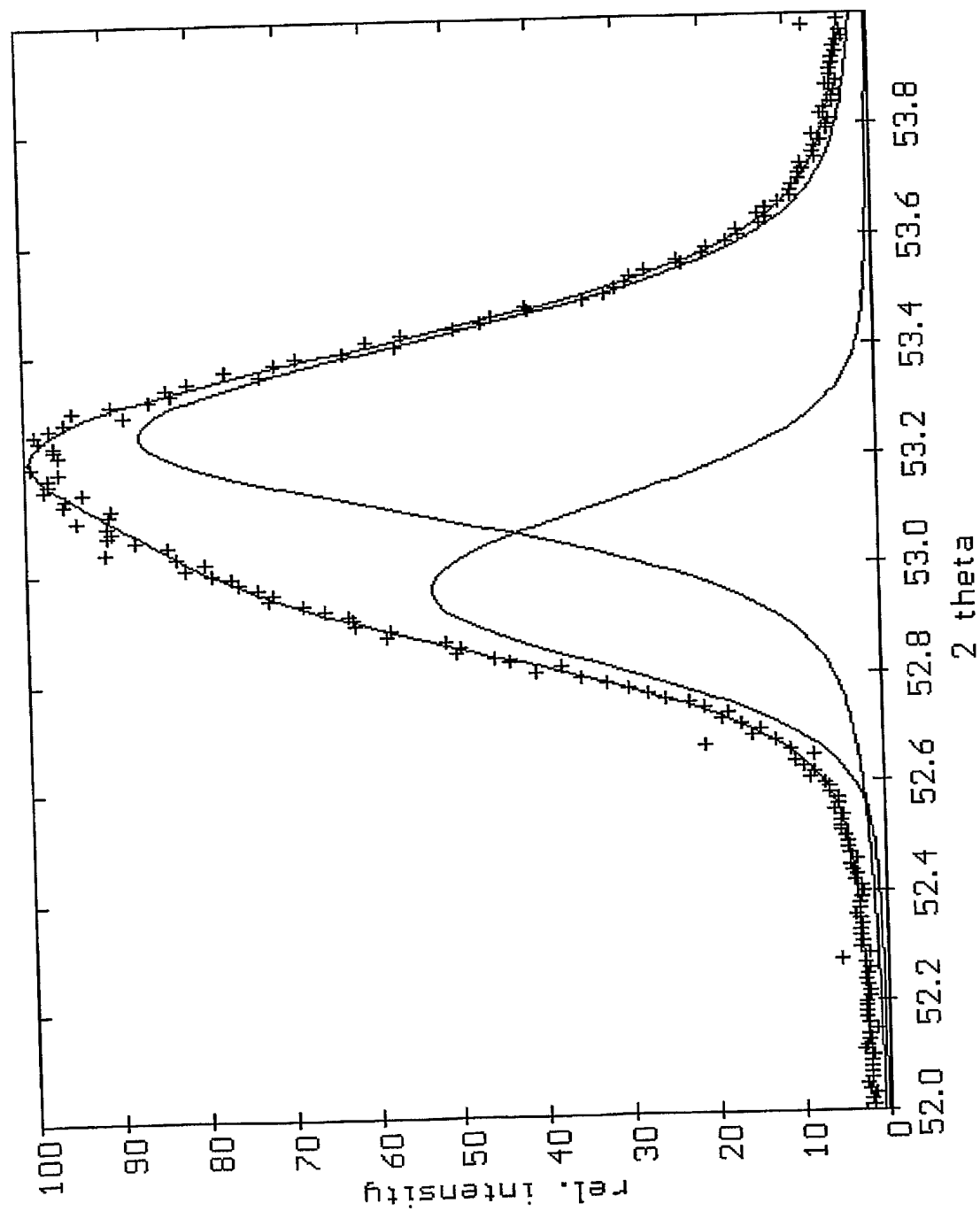
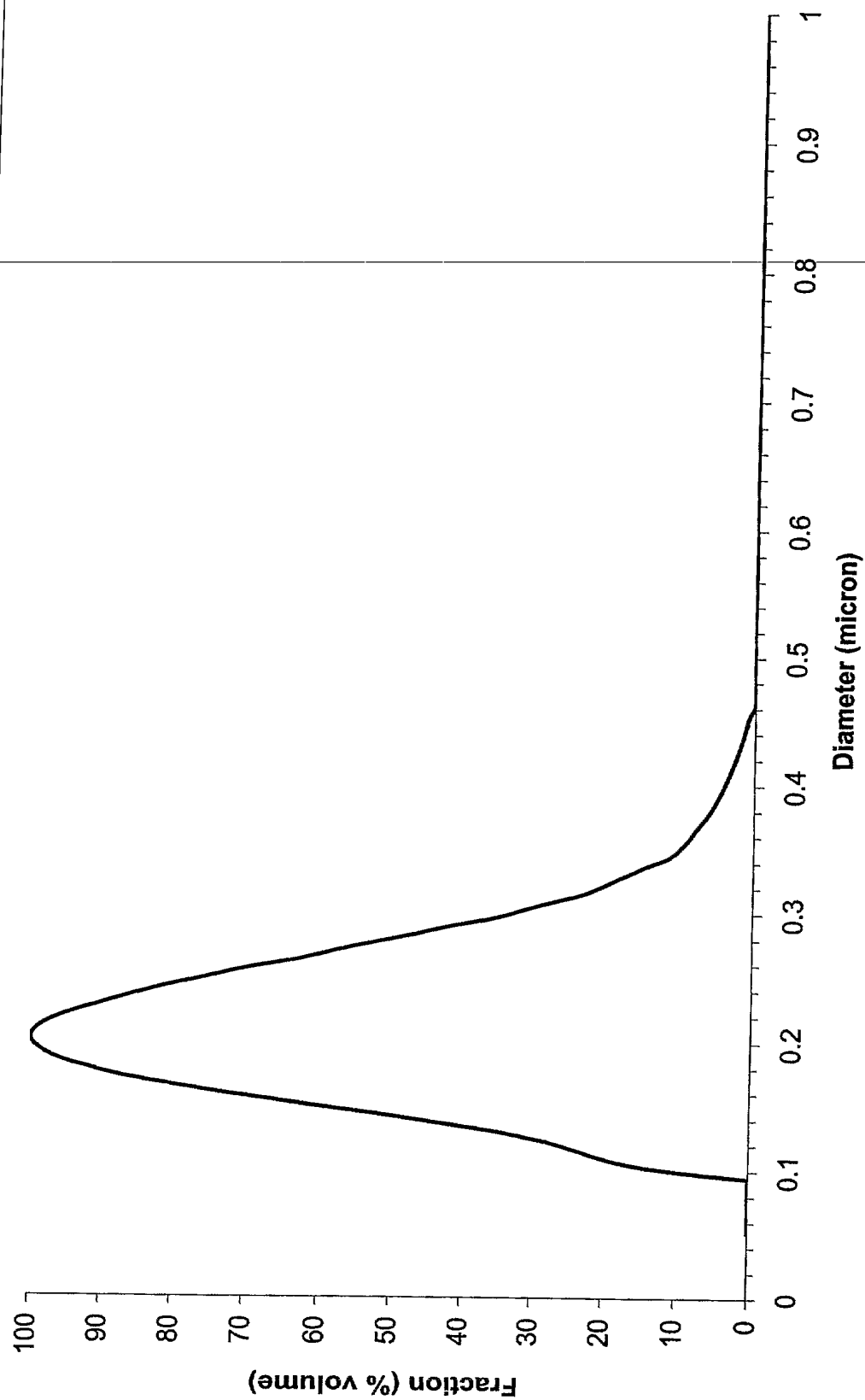


FIGURE 8



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FIGURE 9

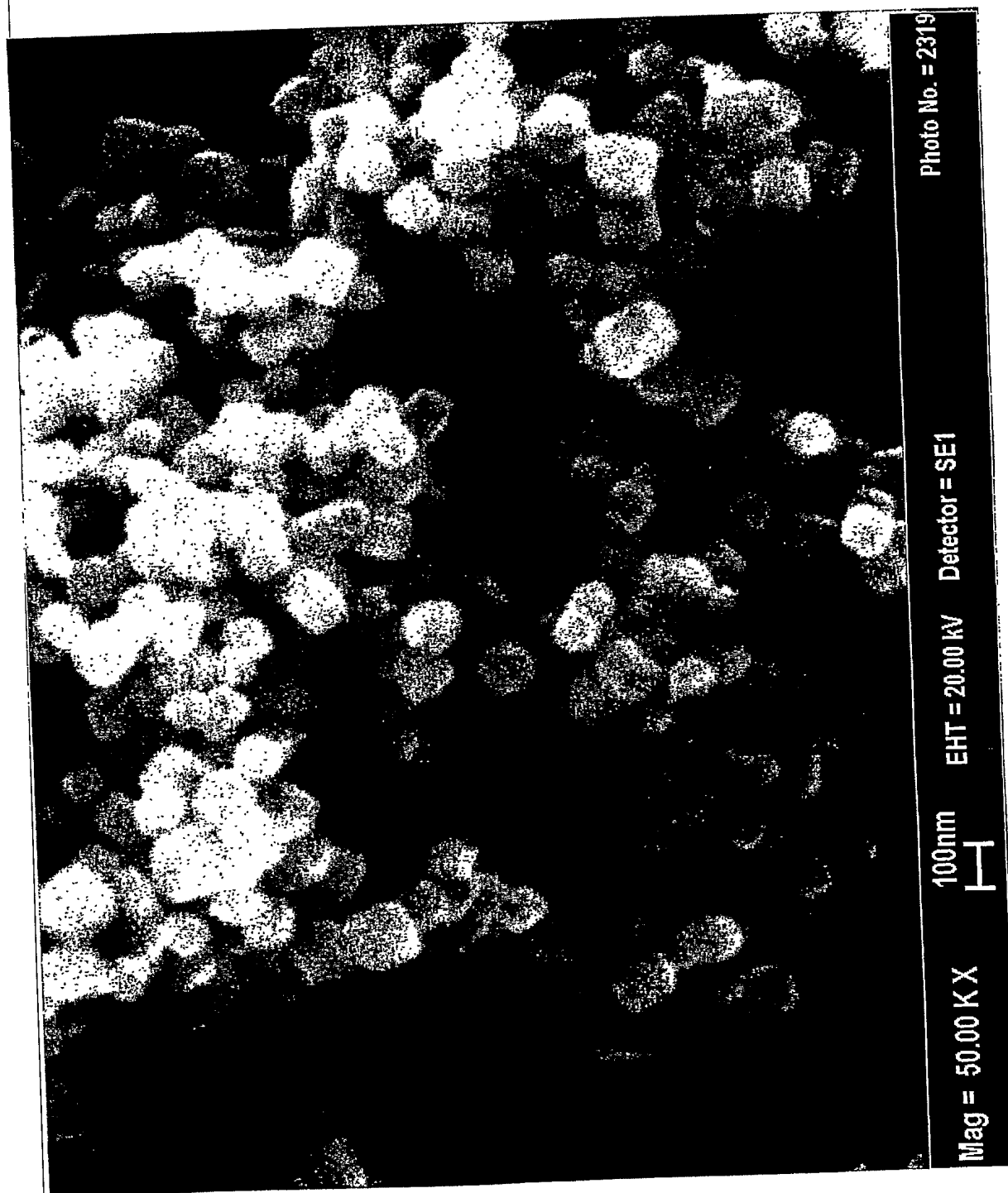


FIGURE 10

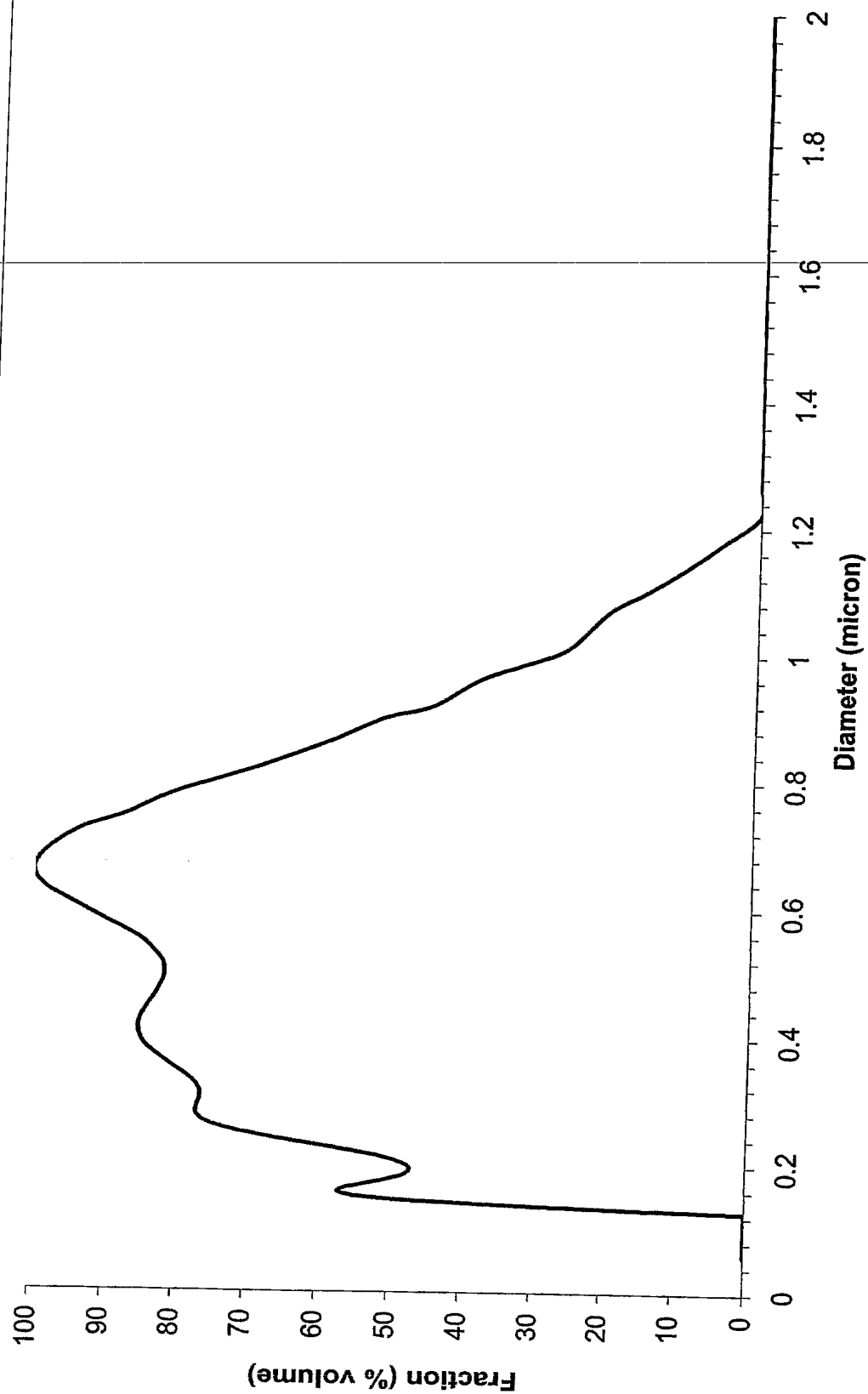


FIGURE 11

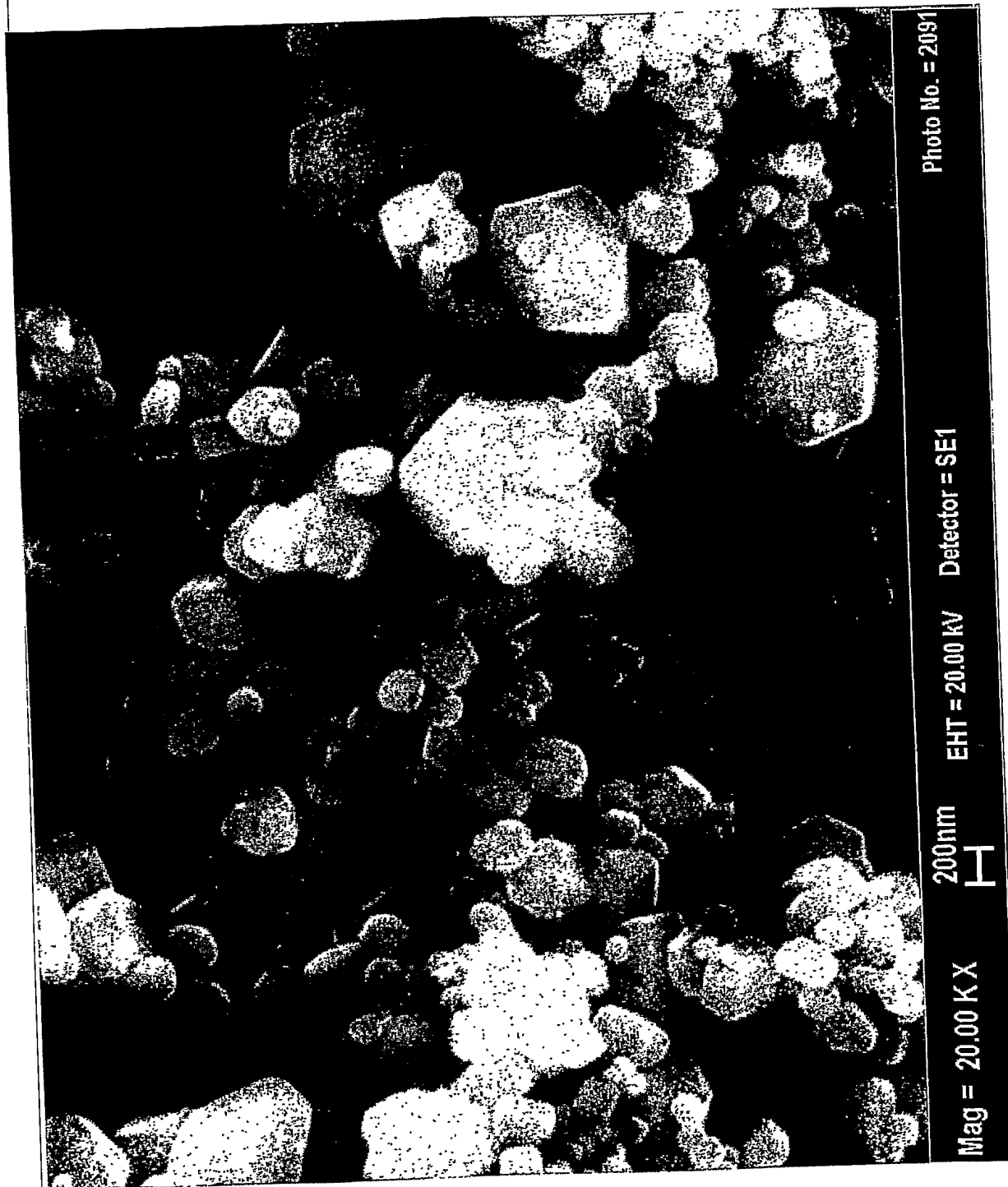
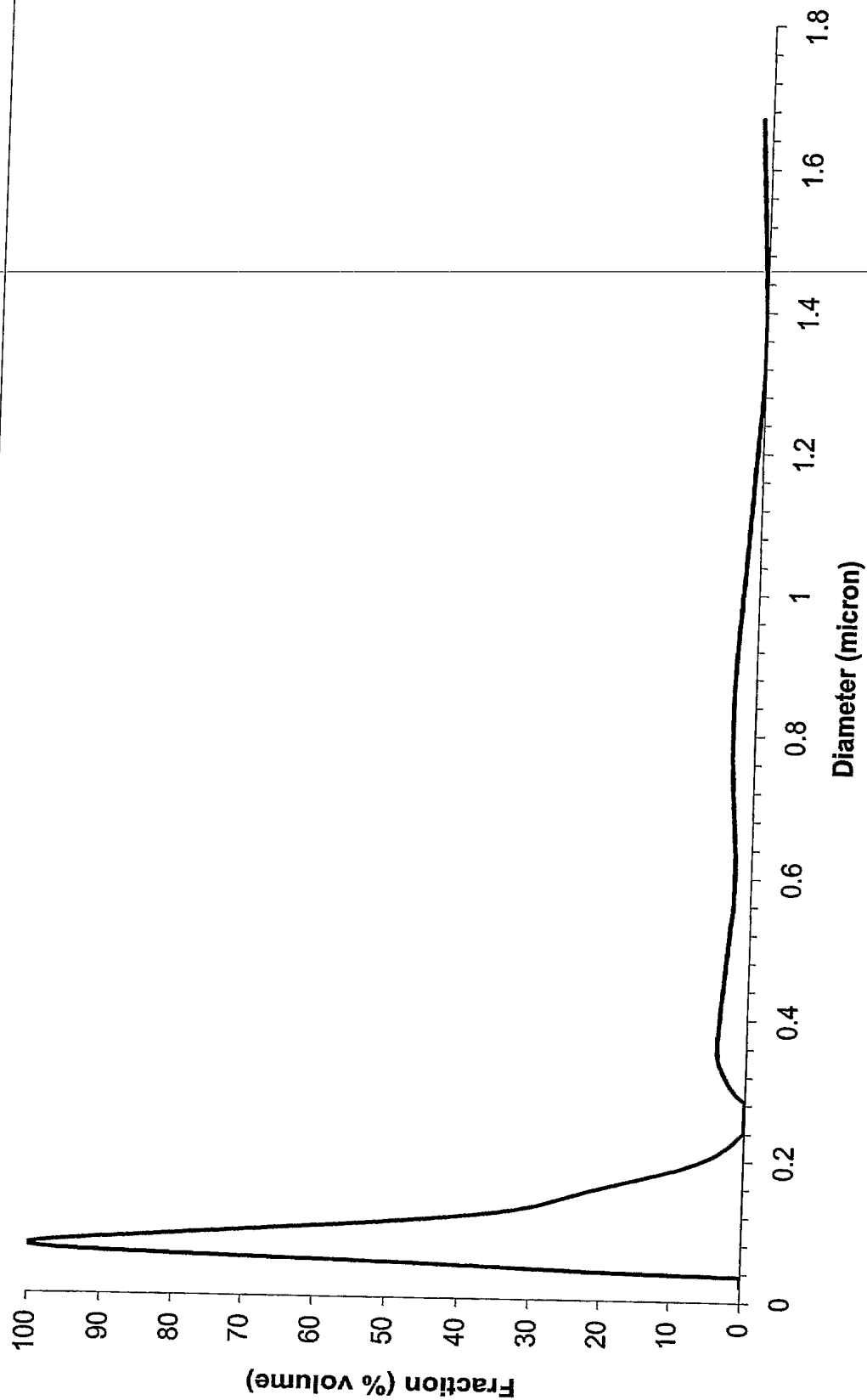


FIGURE 12



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